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**STABILIZED HIGH-SPEED THERMALLY DEVELOPABLE  
EMULSIONS AND PHOTOTHERMOGRAPHIC MATERIALS**

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## **STABILIZED HIGH-SPEED THERMALLY DEVELOPABLE EMULSIONS AND PHOTOTHERMOGRAPHIC MATERIALS**

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### **FIELD OF THE INVENTION**

This invention relates to thermally developable compositions and imaging materials comprising certain polycarboxylic acid compounds. In particular, the invention relates to photothermographic materials containing polycarboxylic acids that have improved shelf stability. The invention also relates to methods of imaging the thermally developable materials.

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### **BACKGROUND OF THE INVENTION**

Silver-containing photothermographic imaging materials (that is, thermally developable photosensitive imaging materials) that are imaged with actinic radiation and then developed using heat and without liquid processing have been known in the art for many years. Such materials are used in a recording process wherein an image is formed by imagewise exposure of the photothermographic material to specific electromagnetic radiation (for example, X-radiation, or ultraviolet, visible, or infrared radiation) and developed by the use of thermal energy. These materials, also known as "dry silver" materials, generally comprise a support having coated thereon: (a) a photocatalyst (that is, a photosensitive compound such as silver halide) that upon such exposure provides a latent image in exposed grains that are capable of acting as a catalyst for the subsequent formation of a silver image in a development step, (b) a relatively or completely non-photosensitive source of reducible silver ions, (c) a reducing composition (usually including a developer) for the reducible silver ions, and (d) a hydrophilic or hydrophobic binder. The latent image is then developed by application of thermal energy.

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In such materials, the photosensitive catalyst is generally a photographic type photosensitive silver halide that is considered to be in catalytic proximity to the non-photosensitive source of reducible silver ions. Catalytic

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proximity requires intimate physical association of these two components either prior to or during the thermal image development process so that when silver atoms ( $\text{Ag}^0$ )<sub>n</sub>, also known as silver specks, clusters, nuclei, or latent image, are generated by irradiation or light exposure of the photosensitive silver halide, those silver atoms are able to catalyze the reduction of the reducible silver ions within a catalytic sphere of influence around the silver atoms [see D. H. Klosterboer, *Imaging Processes and Materials, (Neblette's Eighth Edition)*, J. Sturge, V. Walworth, and A. Shepp, Eds., Van Nostrand-Reinhold, New York, 1989, Chapter 9, pp. 279-291]. It has long been understood that silver atoms act as a catalyst for the reduction of silver ions, and that the photosensitive silver halide can be placed in catalytic proximity with the non-photosensitive source of reducible silver ions in a number of different ways (see, for example, *Research Disclosure*, June 1978, item 17029). Other photosensitive materials, such as titanium dioxide, cadmium sulfide, and zinc oxide have also been reported to be useful in place of silver halide as the photocatalyst in photothermographic materials [see for example, Shepard, *J. Appl. Photog. Eng.* **1982**, 8(5), 210-212, Shigeo et al., *Nippon Kagaku Kaishi*, **1994**, 11, 992-997, and FR 2,254,047 (Robillard)].

The photosensitive silver halide may be made “*in situ*,” for example by mixing a halogen-containing compound such as an inorganic halide or an organic halogen-containing compound with a source of reducible silver ions to achieve partial metathesis and thus causing the *in situ* formation of silver halide ( $\text{AgX}$ ) grains throughout the silver source [see, for example, U.S. Patent 3,457,075 (Morgan et al.)]. In addition, photosensitive silver halides and sources of reducible silver ions can be coprecipitated [see Yu. E. Usanov et al., *J. Imag. Sci. Tech.* **1996**, 40, 104]. Alternatively, a portion of the reducible silver ions can be completely converted to silver halide, and that portion can be added back to the source of reducible silver ions (see Yu. E. Usanov et al., International Conference on Imaging Science, September 7-11, 1998).

The silver halide may also be “preformed” and prepared by an “*ex situ*” process whereby the silver halide ( $\text{AgX}$ ) grains are prepared and grown

separately. With this technique, one has the possibility of controlling the grain size, grain size distribution, dopant levels, and composition much more precisely, so that one can impart more specific properties to both the silver halide grains and the photothermographic material. The preformed silver halide grains may be  
5 introduced prior to and be present during the formation of the source of reducible silver ions. Co-precipitation of the silver halide and the source of reducible silver ions provides a more intimate mixture of the two materials [see for example U.S. Patent 3,839,049 (Simons)]. Alternatively, the preformed silver halide grains may be added to and physically mixed with the source of reducible silver ions.

10           The non-photosensitive source of reducible silver ions is a material that contains reducible silver ions. Typically, the non-photosensitive source of reducible silver ions is a silver salt of a long chain aliphatic carboxylic acid having from 10 to 30 carbon atoms, or mixtures of such salts. Such acids are also known as “fatty acids” or “fatty carboxylic acids.” Silver salts of other organic acids or  
15 other organic compounds, such as silver imidazoles, silver tetrazoles, silver benzotriazoles, silver benzotetrazoles, silver benzothiazoles and silver acetylides may also be used. U.S. Patent 4,260,677 (Winslow et al.) discloses the use of complexes of various inorganic or organic silver salts.

          In photothermographic materials, exposure of the photographic  
20 silver halide to light produces small clusters containing silver atoms ( $\text{Ag}^0$ )<sub>n</sub>. The imagewise distribution of these clusters, known in the art as a latent image, is generally not visible by ordinary means. Thus, the photosensitive material must be further developed to produce a visible image. This is accomplished by the reduction of silver ions that are in catalytic proximity to silver halide grains  
25 bearing the silver-containing clusters of the latent image. This produces a black-and-white image. The non-photosensitive silver source is catalytically reduced to form the visible black-and-white negative image while much of the silver halide, generally, remains as silver halide and is not reduced.

          In photothermographic materials, the reducing agent for the  
30 reducible silver ions, often referred to as a “developer,” may be any compound that, in the presence of the latent image, can reduce silver ion to metallic silver and

is preferably of relatively low activity until it is heated to a temperature sufficient to cause the reaction. A wide variety of classes of compounds have been disclosed in the literature that function as developers for photothermographic materials. At elevated temperatures, the reducible silver ions are reduced by the reducing agent.

5 In photothermographic materials, upon heating, this reaction occurs preferentially in the regions surrounding the latent image. This reaction produces a negative image of metallic silver having a color that ranges from yellow to deep black depending upon the presence of toning agents and other components in the imaging layer(s).

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### **Differences Between Photothermography and Photography**

The imaging arts have long recognized that the field of photothermography is clearly distinct from that of photography. Photothermographic materials differ significantly from conventional silver halide photographic materials that require processing with aqueous processing solutions.

15 As noted above, in photothermographic imaging materials, a visible image is created by heat as a result of the reaction of a developer incorporated within the material. Heating at 50°C or more is essential for this dry development. In contrast, conventional photographic imaging materials require processing in aqueous processing baths at more moderate temperatures (from 30°C to 50°C) to provide a visible image.

20 In photothermographic materials, only a small amount of silver halide is used to capture light and a non-photosensitive source of reducible silver ions (for example a silver carboxylate or a silver benzotriazole) is used to generate the visible image using thermal development. Thus, the imaged photosensitive silver halide serves as a catalyst for the physical development process involving the non-photosensitive source of reducible silver ions and the incorporated reducing agent. In contrast, conventional wet-processed, black-and-white photographic materials use only one form of silver (that is, silver halide) that, upon chemical development, is itself at least partially converted into the silver image, or that upon physical development requires addition of an external silver

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source (or other reducible metal ions that form black images upon reduction to the corresponding metal). Thus, photothermographic materials require an amount of silver halide per unit area that is only a fraction of that used in conventional wet-processed photographic materials.

5                   In photothermographic materials, all of the “chemistry” for imaging is incorporated within the material itself. For example, such materials include a developer (that is, a reducing agent for the reducible silver ions) while conventional photographic materials usually do not. Even in so-called “instant photography,” the developer chemistry is physically separated from the photo-  
10 sensitive silver halide until development is desired. The incorporation of the developer into photothermographic materials can lead to increased formation of various types of “fog” or other undesirable sensitometric side effects. Therefore, much effort has gone into the preparation and manufacture of photothermographic materials to minimize these problems during the preparation of the photothermo-  
15 graphic emulsion as well as during coating, use, storage, and post-processing handling.

Moreover, in photothermographic materials, the unexposed silver halide generally remains intact after development and the material must be stabilized against further imaging and development. In contrast, silver halide is  
20 removed from conventional photographic materials after solution development to prevent further imaging (that is in the aqueous fixing step).

In photothermographic materials, the binder is capable of wide variation and a number of binders (both hydrophilic and hydrophobic) are useful. In contrast, conventional photographic materials are limited almost exclusively to  
25 hydrophilic colloidal binders such as gelatin.

Because photothermographic materials require dry thermal processing, they present distinctly different problems and require different materials in manufacture and use, compared to conventional, wet-processed silver halide photographic materials. Additives that have one effect in conventional  
30 silver halide photographic materials may behave quite differently when incorporated in photothermographic materials where the chemistry is significantly

more complex. The incorporation of such additives as, for example, stabilizers, antifoggants, speed enhancers, supersensitizers, and spectral and chemical sensitizers in conventional photographic materials is not predictive of whether such additives will prove beneficial or detrimental in photothermographic materials. For example, it is not uncommon for a photographic antifoggant useful in conventional photographic materials to cause various types of fog when incorporated into photothermographic materials, or for supersensitizers that are effective in photographic materials to be inactive in photothermographic materials.

These and other distinctions between photothermographic and photographic materials are described in *Imaging Processes and Materials* (Neblette's Eighth Edition), noted above, *Unconventional Imaging Processes*, E. Brinckman et al. (Eds.), The Focal Press, London and New York, 1978, pp. 74-75, in Zou et al., *J. Imaging Sci. Technol.* **1996**, *40*, pp. 94-103, and in M. R. V. Sahyun, *J. Imaging Sci. Technol.* **1998**, *42*, 23.

#### **Problem to be Solved**

The ability of a photothermographic material to be stored without undergoing changes in sensitometric or physical properties is often referred to as "raw-stock keeping" or "natural age keeping." One aspect of improving raw-stock keeping is the control of fog. Photothermographic emulsions, in a manner similar to photographic emulsions and other light-sensitive systems, tend to suffer from fog. Fog is spurious image density that appears in non-imaged areas of the element after development and is often reported in sensitometric results as  $D_{min}$ . In efforts to make more sensitive photothermographic elements, one of the most difficult parameters to control and to maintain at a very low level is the various types of fog or  $D_{min}$ .

As described above, photothermographic materials contain both the image-forming chemistry and the development chemistry in one or more thermally developable imaging layers. During storage and prior to use, the image-forming and development chemistry may degrade or may prematurely chemically react. Later, upon imaging and development, this reaction will be observed as an

increase in  $D_{min}$  in the non-imaged areas. This reaction shortens the shelf-life of photothermographic materials and is often referred to as "shelf-aging fog." A great amount of work has been done to improve the shelf-life characteristics of photothermographic materials. In order to destroy fog centers or to limit their growth during development, additional additives, such as stabilizers and antifoggants, are incorporated into the imaging layers.

There is a continuing need in the industry to reduce shelf-aging fog and thus improve  $D_{min}$  especially in aqueous-based photothermographic materials.

## 10 SUMMARY OF THE INVENTION

The present invention provides a photothermographic composition for providing a black-and-white image, the composition comprising a binder, and in reactive association, a photosensitive silver halide, a non-photosensitive source of reducible silver ions that includes a silver salt of a compound containing an imino group, an ascorbic acid or reductone reducing agent for the non-photosensitive reducible silver ions, and

the composition further comprising a polycarboxylic acid that has a  $pK_a$  of less than 4.5.

In other embodiments, the present invention provides a black-and-white photothermographic material that comprises a support and has on at least one side thereof one or more thermally developable imaging layers comprising a binder and in reactive association, a photosensitive silver halide, a non-photosensitive source of reducible silver ions that includes a silver salt of a compound containing an imino group, an ascorbic acid or a reductone as a reducing agent for the non-photosensitive source reducible silver ions, and optionally an outermost protective layer disposed over the one or more thermally developable imaging layers, and

wherein the outermost surface of the one or more thermally developable imaging layers, or the outermost surface of the protective layer if present, has a surface pH of less than 7, and said one or more thermally



developable imaging layers further comprise a polycarboxylic acid that has a pKa of less than 4.5.

Preferred embodiments comprise a black-and-white aqueous-based photothermographic material that comprises a transparent support having on at least one side thereof:

a) one or more thermally developable imaging layers each comprising a hydrophilic binder that is gelatin, a gelatin derivative, a poly(vinyl alcohol), or a cellulosic material, or is a water-dispersible polymer latex binder, and in reactive association,

a preformed photosensitive silver bromide, silver iodobromide, or a mixture thereof provided predominantly as tabular grains,

a non-photosensitive source of reducible silver ions that includes one or more organic silver salts at least one of which is predominantly a silver salt of benzotriazole,

a reducing composition for the non-photosensitive source of reducible silver ions that includes an ascorbic acid, and

b) optionally an outermost protective layer disposed over said one or more thermally developable imaging layers, and

wherein the outermost surface of the one or more thermally developable imaging layers, or the outermost surface of the protective layer if present, has a surface pH of from about 3 to about 5.5, and the one or more thermally developable imaging layers further comprise citric acid, tricarballic acid, 1,2,3,4-butanetetracarboxylic acid, tartaric acid, succinic acid, phthalic acid, hemimellitic acid, oxalic acid, malonic acid, malic acid, or butyl malonic acid, or mixtures of two or more of these acids, in an amount of from about 0.05 to about 1 mol/mol of silver halide.

Still again, the present invention provides a photothermographic material comprising a support having on a frontside thereof,

a) one or more frontside thermally developable imaging layers comprising a hydrophilic polymer binder or water-dispersible polymer latex binder, and in reactive association, a photosensitive silver halide, a non-photo-

sensitive source of reducible silver ions that includes a silver salt of a compound containing an imino group, an ascorbic acid or reductone as a reducing agent for the non-photosensitive source reducible silver ions, and

the material comprising on the backside of the support, one or more  
5 backside thermally developable imaging layers comprising a hydrophilic polymer binder or a water-dispersible polymer latex binder, and in reactive association, a photosensitive silver halide, a non-photosensitive source of reducible silver ions that includes a silver salt of a compound containing an imino group, and an  
10 reducible silver ions, and

b) optionally an outermost protective layer disposed over the one or more thermally developable imaging layers, and

wherein the one or more thermally developable imaging layers and, the protective layers on both sides of said support if present, have the same or  
15 different composition, and

the material further comprises a polycarboxylic acid that has a pKa of less than 4.5.

The frontside and backside thermally developable layers and compounds of Structure (I) in the frontside and backside layers may have the same  
20 or different compositions.

In the use of the materials of this invention, the present invention provides a method of forming a visible image comprising:

A) imagewise exposing the photothermographic material of the present invention (for example to X-radiation, or electromagnetic radiation in the  
25 visible region) to form a latent image,

B) simultaneously or sequentially, heating the exposed photothermographic material to develop the latent image into a visible image.

This method can be continued where the photothermographic material comprises a transparent support, and the image-forming method further  
30 comprises:

C) positioning the exposed and heat-developed photothermographic material with the visible image therein between a source of imaging radiation and an imageable material that is sensitive to the imaging radiation, and

D) exposing the imageable material to the imaging radiation through  
5 the visible image in the exposed and heat-developed photothermographic material to provide an image in the imageable material.

Further, the present invention provides an imaging assembly comprising the photothermographic material of the present invention that is arranged in association with one or more phosphor intensifying screens for use  
10 during imaging. The imaging assembly can be exposed to imaging X-radiation to excite the phosphors that then provide a latent image in the photothermographic material. In these embodiments, the photothermographic material may include one or more thermally developable layers on both sides of the support.

The present invention provides a number of advantages with the  
15 use of the polycarboxylic acid compounds defined herein in combination with specific reducing agents. They can be used in a variety of thermally developable materials and particularly in aqueous-based photothermographic materials. They are particularly useful in aqueous-based photothermographic materials wherein the organic silver salt is a salt of a compound containing an imino group (such as  
20 silver benzotriazole) and have been observed to reduce changes in  $D_{min}$ ,  $D_{max}$ , and photospeed upon storage. Without defining a mechanism for use of the polycarboxylic acid compounds, it is believed that these compounds act as silver scavengers or silver coordinating agents that prevent silver catalysis of further development and thus provide desirable natural age keeping results.

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#### **DETAILED DESCRIPTION OF THE INVENTION**

The photothermographic materials of this invention can be used in black-and-white or color photothermography and in electronically generated black-and-white or color hardcopy recording. They can be used in microfilm  
30 applications, in radiographic imaging (for example digital medical imaging), X-ray radiography, and in industrial radiography. Furthermore, the absorbance of these

photothermographic materials between 350 and 450 nm is desirably low (less than 0.5), to permit their use in the graphic arts area (for example, imagesetting and phototypesetting), in the manufacture of printing plates, in contact printing, in duplicating ("duping"), and in proofing.

5           The photothermographic materials of this invention are particularly useful for medical imaging of human or animal subjects in response to visible or X-radiation for use in medical diagnosis. Such applications include, but are not limited to, thoracic imaging, mammography, dental imaging, orthopedic imaging, general medical radiography, therapeutic radiography, veterinary radiography, and  
10 auto-radiography. When used with X-radiation, the photothermographic materials of this invention may be used in combination with one or more phosphor intensifying screens, with phosphors incorporated within the photothermographic emulsion, or with a combination thereof. Such materials are particularly useful for dental radiography. The materials of this invention are also useful for non-medical  
15 uses of visible or X-radiation (such as X-ray lithography and industrial radiography).

          The photothermographic materials of this invention can be made sensitive to radiation of any suitable wavelength. Thus, in some embodiments, the materials are sensitive at ultraviolet, visible, near infrared, or infrared wave-  
20 lengths, of the electromagnetic spectrum. In these embodiments, the materials are preferably sensitive to radiation greater than 350 nm (such as sensitivity to, from about 350 nm to about 450 nm). Increased sensitivity to a particular region of the spectrum is imparted through the use of various sensitizing dyes.

          The photothermographic materials of this invention are also useful  
25 for non-medical uses of visible or X-radiation (such as X-ray lithography and industrial radiography). In such imaging applications, it is particularly desirable that the photothermographic materials be "double-sided."

          In the photothermographic materials of this invention, the components needed for imaging can be in one or more photothermographic layers  
30 on one side ("frontside") of the support. The layer(s) that contain the photo-sensitive photocatalyst (such as a photosensitive silver halide) or the non-photo-

sensitive source of reducible silver ions, or both, are referred to herein as photo-thermographic emulsion layer(s). The photocatalyst and the non-photosensitive source of reducible silver ions are in catalytic proximity (that is, in reactive association with each other) and preferably are in the same emulsion layer.

5                   Where the materials contain imaging layers on one side of the support only, various non-imaging layers are usually disposed on the “backside” (non-emulsion or non-imaging side) of the materials, including, antihalation layer(s), protective layers, antistatic layers, and transport enabling layers.

10                   In such instances, various non-imaging layers can also be disposed on the “frontside” or imaging or emulsion side of the support, including protective topcoat layers, primer layers, interlayers, opacifying layers, antistatic layers, antihalation layers, acutance layers, auxiliary layers, and other layers readily apparent to one skilled in the art.

15                   For some embodiments it may be useful that the photothermographic materials be “double-sided” and have photothermographic coatings on both sides of the support. Such constructions can also include one or more protective topcoat layers, primer layers, interlayers, antistatic layers, acutance layers, antihalation layers, auxiliary layers, anti-crossover layers, and other layers readily apparent to one skilled in the art on either or both sides of the support.

20                   When the photothermographic materials of this invention are heat-developed as described below in a substantially water-free condition after, or simultaneously with, imagewise exposure, a silver image (preferably a black-and-white silver image) is obtained.

## 25   **Definitions**

As used herein:

In the descriptions of the photothermographic materials of the present invention, “a” or “an” component refers to “at least one” of that component [for example, the polycarboxylic acid compounds of Structure (I)].

30                   Heating in a substantially water-free condition as used herein, means heating at a temperature of from about 50°C to about 250°C with little

more than ambient water vapor present. The term “substantially water-free condition” means that the reaction system is approximately in equilibrium with water in the air and water for inducing or promoting the reaction is not particularly or positively supplied from the exterior to the material. Such a condition is  
5 described in T. H. James, *The Theory of the Photographic Process*, Fourth Edition, Eastman Kodak Company, Rochester, NY, 1977, p. 374.

“Photothermographic material(s)” means a construction comprising at least one photothermographic emulsion layer or a photothermographic set of emulsion layers (wherein the photosensitive silver halide and the source of  
10 reducible silver ions are in one layer and the other essential components or desirable additives are distributed, as desired, in the same layer or in an adjacent coating layer) as well as any supports, topcoat layers, image-receiving layers, blocking layers, antihalation layers, subbing or priming layers. These materials also include multilayer constructions in which one or more imaging components  
15 are in different layers, but are in “reactive association” so that they readily come into contact with each other during coating, imaging, and/or development. For example, one layer can include the non-photosensitive source of reducible silver ions and another layer can include the reducing composition, but the two reactive components are in reactive association with each other.

20 When used in photothermography, the term, “imagewise exposing” or “imagewise exposure” means that the material is imaged using any exposure means that provides a latent image using electromagnetic radiation. This includes, for example, by analog exposure where an image is formed by projection onto the photosensitive material as well as by digital exposure where the image is formed  
25 one pixel at a time such as by modulation of scanning laser radiation.

“Catalytic proximity” or “reactive association” means that the materials are in the same layer or in adjacent layers so that they readily come into contact with each other during thermal imaging and development.

“Emulsion layer,” “imaging layer,” or “photothermographic  
30 emulsion layer,” means a layer of a photothermographic material that contains the photosensitive silver halide and/or non-photosensitive source of reducible silver

ions. It can also mean a layer of the photothermographic material that contains, in addition to the photosensitive silver halide and/or non-photosensitive source of reducible ions, additional essential components and/or desirable additives. These layers are usually on what is known as the “frontside” of the support.

5                   In addition, “frontside” also generally means the side of a thermally developable material that is first exposed to imaging radiation, and “backside” generally refers to the opposite side of the thermally developable material.

                  The terms “double-sided” and “double-faced coating” are used to define photothermographic materials having one or more of the same or different  
10 thermally developable emulsion layers disposed on both sides (frontside and backside) of the support. Another term for double-sided is “duplitzed.”

                  “Photocatalyst” means a photosensitive compound such as silver halide that, upon exposure to radiation, provides a compound that is capable of acting as a catalyst for the subsequent development of the image-forming material.

15                   Many of the materials used herein are provided as a solution. The term “active ingredient” means the amount or the percentage of the desired material contained in a sample. All amounts listed herein are the amount of active ingredient added.

                  “Ultraviolet region of the spectrum” refers to that region of the  
20 spectrum less than or equal to 410 nm, and preferably from about 100 nm to about 410 nm, although parts of these ranges may be visible to the naked human eye. More preferably, the ultraviolet region of the spectrum is the region of from about 190 nm to about 405 nm.

                  “Visible region of the spectrum” refers to that region of the  
25 spectrum of from about 400 nm to about 700 nm.

                  “Short wavelength visible region of the spectrum” refers to that region of the spectrum of from about 400 nm to about 450 nm.

                  “Red region of the spectrum” refers to that region of the spectrum of from about 600 nm to about 700 nm.

30                   “Infrared region of the spectrum” refers to that region of the spectrum of from about 700 nm to about 1400 nm.

“Non-photosensitive” means not intentionally light sensitive.

The sensitometric terms  $D_{\min}$  and  $D_{\max}$  have conventional definitions known in the imaging arts. In photothermographic materials,  $D_{\min}$  is considered herein as image density achieved when the photothermographic material is thermally developed without prior exposure to radiation. It is the  
5 average of eight lowest density values on the exposed side of the fiducial mark.

The sensitometric term “absorbance” is another term for optical density (OD).

“Transparent” means capable of transmitting visible light or  
10 imaging radiation without appreciable scattering or absorption.

As used herein, the phrase “organic silver coordinating ligand” refers to an organic molecule capable of forming a bond with a silver atom. Although the compounds so formed are technically silver coordination compounds they are also often referred to as silver salts.

15 In the compounds described herein, no particular double bond geometry (for example, *cis* or *trans*) is intended by the structures drawn. Similarly, in compounds having alternating single and double bonds and localized charges their structures are drawn as a formalism. In reality, both electron and charge delocalization exists throughout the conjugated chain.

20 As is well understood in this art, for the chemical compounds herein described, substitution is not only tolerated, but is often advisable and various substituents are anticipated on the compounds used in the present invention unless otherwise stated. Thus, when a compound is referred to as “having the structure” of, or as “a derivative” of, a given formula, any substitution  
25 that does not alter the bond structure of the formula or the shown atoms within that structure is included within the formula, unless such substitution is specifically excluded by language (such as “free of carboxy-substituted alkyl”).

As a means of simplifying the discussion and recitation of certain substituent groups, the term “group” refers to chemical species that may be  
30 substituted as well as those that are not so substituted. Thus, the term “group,” such as “alkyl group” is intended to include not only pure hydrocarbon alkyl



chains, such as methyl, ethyl, *n*-propyl, *t*-butyl, cyclohexyl, *iso*-octyl, and octadecyl, but also alkyl chains bearing substituents known in the art, such as hydroxyl, alkoxy, phenyl, halogen atoms (F, Cl, Br, and I), cyano, nitro, amino, and carboxy. For example, alkyl group includes ether and thioether groups (for  
5 example CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O-CH<sub>2</sub>- and CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-S-CH<sub>2</sub>-), hydroxyalkyl (such as 1,2-dihydroxyethyl), haloalkyl, nitroalkyl, alkylcarboxy, carboxyalkyl, carboxamido, sulfoalkyl, and other groups readily apparent to one skilled in the art. Substituents that adversely react with other active ingredients, such as very strongly electrophilic or oxidizing substituents, would, of course, be excluded by  
10 the ordinarily skilled artisan as not being inert or harmless.

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15 Other aspects, advantages, and benefits of the present invention are apparent from the detailed description, examples, and claims provided in this application.

### **The Photocatalyst**

20 As noted above, the photothermographic materials of the present invention include one or more photocatalysts in the photothermographic emulsion layer(s). Useful photocatalysts are typically photosensitive silver halides such as silver bromide, silver iodide, silver chloride, silver bromiodide, silver chloro-  
bromiodide, silver chlorobromide, and others readily apparent to one skilled in  
25 the art. Mixtures of silver halides can also be used in any suitable proportion. In preferred embodiments, the silver halide comprises at least 70 mol% silver bromide with the remainder being silver chloride and silver iodide. More preferably, the amount of silver bromide is at least 90 mol%. Silver bromide and silver bromiodide are more preferred silver halides, with the latter silver halide  
30 having up to 10 mol% silver iodide based on total silver halide.

In some embodiments of aqueous-based photothermographic materials, higher amounts of iodide may be present in the photosensitive silver halide grains, and particularly from about 20 mol % up to the saturation limit of iodide, to increase image stability and to reduce “print-out,” as described for  
5 example in copending and commonly assigned U.S. Serial No. 10/246,265 (filed September 18, 2002 by Maskasky and Scaccia).

The shape (morphology) of the photosensitive silver halide grains used in the present invention need not be limited. The silver halide grains may have any crystalline habit including, but not limited to, cubic, octahedral,  
10 tetrahedral, orthorhombic, rhombic, dodecahedral, other polyhedral, tabular, laminar, twinned, or platelet morphologies and may have epitaxial growth of crystals thereon. If desired, a mixture of these crystals can be employed. Silver halide grains having cubic and tabular morphology are preferred, and mixtures of both cubic and tabular grains can be used in the present invention. More  
15 preferably, the silver halide grains are predominantly (at least 50% based on total silver halide) present as tabular grains.

The silver halide grains may have a uniform ratio of halide throughout. They may have a graded halide content, with a continuously varying ratio of, for example, silver bromide and silver iodide or they may be of the  
20 core-shell type, having a discrete core of one or more silver halides, and a discrete shell of one of more different silver halides. For example, the central regions of the tabular grains may contain at least 1 mol % more iodide than the outer or annular regions of the grains. Core-shell silver halide grains useful in photothermographic materials and methods of preparing these materials are described  
25 for example in U.S. Patent 5,382,504 (Shor et al.), incorporated herein by reference. Iridium and/or copper doped core-shell and non-core-shell grains are described in U.S. Patent 5,434,043 (Zou et al.) and U.S. Patent 5,939,249 (Zou), both incorporated herein by reference. Mixtures of preformed silver halide grains having different compositions or dopants may be employed.

30 In some instances, it may be helpful to prepare the photosensitive silver halide grains in the presence of a hydroxytetraazaindene (such as 4-hydroxy-

6-methyl-1,3,3a,7-tetraazaindene) or an N-heterocyclic compound comprising at least one mercapto group (such as 1-phenyl-5-mercaptotetrazole) to provide increased photospeed. Details of this procedure are provided in U.S. Patent 6,413,710 (Shor et al.), that is incorporated herein by reference.

5           The photosensitive silver halide can be added to (or formed within) the emulsion layer(s) in any fashion as long as it is placed in catalytic proximity to the non-photosensitive source of reducible silver ions.

          It is preferred that the silver halide grains be preformed and prepared by an *ex-situ* process. The silver halide grains prepared *ex-situ* may then  
10   be added to and physically mixed with the non-photosensitive source of reducible silver ions.

          In some formulations it is useful to form the source of reducible silver ions in the presence of *ex-situ*-prepared silver halide. In this process, the source of reducible silver ions, such as a silver salt of an imino compound, is  
15   formed in the presence of the preformed silver halide grains. Co-precipitation of the reducible source of silver ions in the presence of silver halide provides a more intimate mixture of the two materials [see, for example U.S. Patent 3,839,049 (Simons)]. Materials of this type are often referred to as “preformed emulsions.”

          In general, the non-tabular silver halide grains used in the imaging  
20   formulations can vary in average diameter of up to several micrometers ( $\mu\text{m}$ ) depending on their desired use. Usually, the silver halide grains have an average particle size of from about 0.01 to about 1.5  $\mu\text{m}$ . In some embodiments, the average particle size is preferable from about 0.03 to about 1.0  $\mu\text{m}$ , and more preferably from about 0.05 to about 0.8  $\mu\text{m}$ . Those of ordinary skill in the art  
25   understand that there is a finite lower practical limit for silver halide grains that is partially dependent upon the wavelengths to which the grains are spectrally sensitized. Such a lower limit, for example, is typically from about 0.01 to about 0.005  $\mu\text{m}$ .

          The average size of the photosensitive doped silver halide grains is  
30   expressed by the average diameter if the grains are spherical, and by the average of

the diameters of equivalent circles for the projected images if the grains are cubic, tabular, or other non-spherical shapes.

Grain size may be determined by any of the methods commonly employed in the art for particle size measurement. Representative methods are described by in “Particle Size Analysis,” ASTM Symposium on Light Microscopy, 5 R. P. Loveland, 1955, pp. 94-122, and in C. E. K. Mees and T. H. James, *The Theory of the Photographic Process*, Third Edition, Macmillan, New York, 1966, Chapter 2. Particle size measurements may be expressed in terms of the projected areas of grains or approximations of their diameters. These will provide 10 reasonably accurate results if the grains of interest are substantially uniform in shape.

In most preferred embodiments of this invention, the silver halide grains are provided predominantly (based on at least 50 mol % silver) as tabular silver halide grains that are considered “ultrathin” and have an average thickness 15 of at least 0.02  $\mu\text{m}$  and up to and including 0.10  $\mu\text{m}$ . Preferably, these ultrathin grains have an average thickness of at least 0.03  $\mu\text{m}$  and more preferably of at least 0.04  $\mu\text{m}$ , and up to and including 0.08  $\mu\text{m}$  and more preferably up to and including 0.07  $\mu\text{m}$ .

In addition, these ultrathin tabular grains have an equivalent 20 circular diameter (ECD) of at least 0.5  $\mu\text{m}$ , preferably at least 0.75  $\mu\text{m}$ , and more preferably at least 1  $\mu\text{m}$ . The ECD can be up to and including 8  $\mu\text{m}$ , preferably up to and including 6  $\mu\text{m}$ , and more preferably up to and including 4  $\mu\text{m}$ .

The aspect ratio of the useful tabular grains is at least 5:1, preferably at least 10:1, and more preferably at least 15:1. For practical purposes, 25 the tabular grain aspect is generally up to 50:1.

The grain size of ultrathin tabular grains may be determined by any of the methods commonly employed in the art for particle size measurement, such as those described above.

The ultrathin tabular silver halide grains can also be doped using 30 one or more of the conventional metal dopants known for this purpose including those described in *Research Disclosure* item 38957, September, 1996 and U.S.

Patent 5,503,970 (Olm et al.), incorporated herein by reference. Preferred dopants include iridium (III or IV) and ruthenium (II or III) salts.

Preformed silver halide emulsions used in the material of this invention can be prepared by aqueous or organic processes and can be unwashed  
5 or washed to remove soluble salts. In the latter case, the soluble salts can be removed by ultrafiltration, by chill setting and leaching, or by washing the coagulum [for example, by the procedures described in U.S. Patent 2,618,556 (Hewitson et al.), U.S. Patent 2,614,928 (Yutzy et al.), U.S. Patent 2,565,418 (Yackel), U.S. Patent 3,241,969 (Hart et al.), and U.S. Patent 2,489,341 (Waller et  
10 al.)].

It is also effective to use an *in-situ* process in which a halide-containing compound is added to an organic silver salt to partially convert the silver of the organic silver salt to silver halide. The compound can be one or more  
15 inorganic halides (such as zinc bromide, calcium bromide, lithium bromide, or zinc iodide) or an organic halogen-containing compound (such as N-bromo-succinimide or pyridinium hydrobromide perbromide). A portion of the silver halide grains used in the present invention can be prepared using an *in-situ* process. The details of such *in-situ* generation of silver halide are well known and described for example in U.S. Patent 3,457,075 (Morgan et al.).

20 Additional methods of preparing these silver halide and organic silver salts and manners of blending them are described in *Research Disclosure*, June 1978, item 17029, U.S. Patent 3,700,458 (Lindholm) and U.S. Patent 4,076,539 (Ikenoue et al.), JP Kokai 49-013224, (Fuji), JP Kokai 50-017216 (Fuji), and JP Kokai 51-042529 (Fuji).

25 Mixtures of both *in-situ* and *ex-situ* silver halide grains may be used.

The one or more light-sensitive silver halides used in the photo-thermographic materials of the present invention are preferably present in an amount of from about 0.005 to about 0.5 mole, more preferably from about 0.01 to  
30 about 0.25 mole, and most preferably from about 0.03 to about 0.15 mole, per mole of non-photosensitive source of reducible silver ions.

### Chemical Sensitizers

The photosensitive silver halides used in photothermographic features of the invention may be employed without modification. However, one or  
5 more conventional chemical sensitizers may be used in the preparation of the photosensitive silver halides to increase photospeed. Such compounds may contain sulfur, tellurium, or selenium, or may comprise a compound containing gold, platinum, palladium, ruthenium, rhodium, iridium, or combinations thereof, a reducing agent such as a tin halide or a combination of any of these. The details  
10 of these materials are provided for example, in T. H. James, *The Theory of the Photographic Process*, Fourth Edition, Eastman Kodak Company, Rochester, NY, 1977, Chapter 5, pp. 149-169. Suitable conventional chemical sensitization procedures are also described in U.S. Patent 1,623,499 (Sheppard et al.), U.S. Patent 2,399,083 (Waller et al.), U.S. Patent 3,297,447 (McVeigh), U.S. Patent  
15 3,297,446 (Dunn), U.S. Patent 5,049,485 (Deaton), U.S. Patent 5,252,455 (Deaton), U.S. Patent 5,391,727 (Deaton), U.S. Patent 5,912,111 (Lok et al.), U.S. Patent 5,759,761 (Lushington et al.), U.S. Patent 6,296,998 (Eikenberry et al), and EP 0 915 371 A1 (Lok et al.).

In addition, mercaptotetrazoles and tetraazaindenes as described in  
20 U.S. Patent 5,691,127 (Daubendiek et al.), incorporated herein by reference, can be used as suitable addenda for tabular silver halide grains.

When used, sulfur sensitization is usually performed by adding a sulfur sensitizer and stirring the emulsion at an appropriate temperature for a predetermined time. Various sulfur compounds can be used. Some examples of  
25 sulfur sensitizers include thiosulfates, thioureas, thioamides, thiazoles, rhodanines, phosphine sulfides, thiohydantoin, 4-oxo-oxazolidine-2-thiones, dipolysulfides, mercapto compounds, polythionates, and elemental sulfur.

Certain tetrasubstituted thiourea compounds are also useful in the present invention. Such compounds are described, for example in U.S. Patent  
30 6,296,998 (Eikenberry et al.) and U.S. Patent 6,322,961 (Lam et al.). Also useful are the tetrasubstituted middle chalcogen (that is, sulfur, selenium, and tellurium)

thiourea compounds disclosed in U.S. Patent 4,810,626 (Burgmaier et al.). All of the above publications are incorporated herein by reference.

The amount of sulfur sensitizer to be added varies depending upon various conditions such as pH, temperature and grain size of silver halide at the  
5 time of chemical ripening, it is preferably from  $10^{-7}$  to  $10^{-2}$  mole per mole of silver halide, and more preferably from  $10^{-6}$  to  $10^{-4}$  mole per mold of silver halide.

Still other useful chemical sensitizers include certain selenium-containing compounds. When used, selenium sensitization is usually performed by adding a selenium sensitizer and stirring the emulsion at an appropriate  
10 temperature for a predetermined time. Some specific examples of useful selenium compounds can be found in U.S. Patents 5,158,892 (Sasaki et al.), 5,238,807 (Sasaki et al.), 5,942,384 (Arai et al.) and in co-pending and commonly assigned U.S. Patent 6,620,577 (Lynch et al.). All of the above documents are incorporated herein by reference.

15 Still other useful chemical sensitizers include certain tellurium-containing compounds. When used, tellurium sensitization is usually performed by adding a tellurium sensitizer and stirring the emulsion at an appropriate temperature for a predetermined time. Tellurium compounds for use as chemical sensitizers can be selected from those described in *J. Chem. Soc., Chem. Commun.*  
20 **1980**, 635, *ibid.*, **1979**, 1102, *ibid.*, **1979**, 645, *J. Chem. Soc. Perkin. Trans*, **1980**, *1*, 2191, *The Chemistry of Organic Selenium and Tellurium Compounds*, S. Patai and Z. Rappoport, Eds., Vol. 1 (1986), and Vol. 2 (1987), U.S. Patent 1,623,499 (Sheppard et al.), U.S. Patent 3,320,069 (Illingsworth), U.S. Patent 3,772,031 (Berry et al.), U.S. Patent 5,215,880 (Kojima et al.), U.S. Patent 5,273,874  
25 (Kojima et al.), U.S. Patent 5,342,750 (Sasaki et al.), U. S. Patent 5,677,120 (Lushington et al.), British Patent 235,211 (Sheppard), British Patent 1,121,496 (Halwig), British Patent 1,295,462 (Hilson et al.) British Patent 1,396,696 (Simons), JP Kokai 04-271341 A (Morio et al.), in co-pending and commonly assigned U.S. Published Application 2002-0164549 (Lynch et al.), and in  
30 co-pending and commonly assigned U.S. Published Application 2003-0073026 (Gylsing et al.). All of the above documents are incorporated herein by reference.

The amount of the selenium or tellurium sensitizer used in the present invention varies depending on silver halide grains used or chemical ripening conditions. However, it is generally from  $10^{-8}$  to  $10^{-2}$  mole per mole of silver halide, preferably on the order of from  $10^{-7}$  to  $10^{-3}$  mole of silver halide.

5           Noble metal sensitizers for use in the present invention include gold, platinum, palladium and iridium. Gold sensitization is particularly preferred.

When used, the gold sensitizer used for the gold sensitization of the silver halide emulsion used in the present invention may have an oxidation number of 1 or 3, and may be a gold compound commonly used as a gold  
10   sensitizer. U.S. Patent 5,858,637 (Eshelman et al.) describes various gold(I) compounds that can be used as chemical sensitizers. Other useful gold compounds can be found in U. S. Patent 5,759,761 (Lushington et al.). Useful combinations of gold(I) complexes and rapid sulfiding agents are described in U.S. Patent 6,322,961 (Lam et al.). Combinations of gold(III) compounds and  
15   either sulfur- or tellurium-containing compounds are useful as chemical sensitizers and are described in U.S. Patent 6,423,481 (Simpson et al.). All of the above references are incorporated herein by reference.

Reduction sensitization may also be used. Specific examples of compounds useful in reduction sensitization include, but are not limited to,  
20   stannous chloride, hydrazine ethanolamine, and thioureaoxide. Reduction sensitization may be performed by ripening the grains while keeping the emulsion at pH 7 or above, or at pAg 8.3 or less.

The chemical sensitizers can be used in making the silver halide emulsions in conventional amounts that generally depend upon the average size of  
25   the silver halide grains. Generally, the total amount is at least  $10^{-10}$  mole per mole of total silver, and preferably from about  $10^{-8}$  to about  $10^{-2}$  mole per mole of total silver. The upper limit can vary depending upon the compound(s) used, the level of silver halide, and the average grain size and grain morphology, and would be readily determinable by one of ordinary skill in the art.



### Spectral Sensitizers

The photosensitive silver halides used in the photothermographic features of the invention may be spectrally sensitized with various spectral sensitizing dyes that are known to enhance silver halide sensitivity to ultraviolet, visible, and/or infrared radiation. Non-limiting examples of sensitizing dyes that can be employed include cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, holopolar cyanine dyes, hemicyanine dyes, styryl dyes, and hemioxanol dyes. Cyanine dyes, merocyanine dyes and complex merocyanine dyes are particularly useful. Spectral sensitizing dyes are chosen for optimum photosensitivity, stability, and ease of synthesis. They may be added at any stage in chemical finishing of the photothermographic emulsion.

Suitable sensitizing dyes such as those described in U.S. Patent 3,719,495 (Lea), U.S. Patent 4,396,712 (Kinoshita et al.), U.S. Patent 4,439,520 (Kofron et al.), U.S. Patent 4,690,883 (Kubodera et al.), U.S. Patent 4,840,882 (Iwagaki et al.), U.S. Patent 5,064,753 (Kohno et al.), U.S. Patent 5,281,515 (Delprato et al.), U.S. Patent 5,393,654 (Burrows et al.), U.S. Patent 5,441,866 (Miller et al.), U.S. Patent 5,508,162 (Dankosh), U.S. Patent 5,510,236 (Dankosh), U.S. Patent 5,541,054 (Miller et al.), JP Kokai 2000-063690 (Tanaka et al.), JP Kokai 2000-112054 (Fukusaka et al.), JP Kokai 2000-273329 (Tanaka et al.), JP Kokai 2001-005145 (Arai), JP Kokai 2001-064527 (Oshiyama et al.), and JP Kokai 2001-154305 (Kita et al.), can be used in the practice of the invention. All of the publications noted above are incorporated herein by reference.

A summary of generally useful spectral sensitizing dyes is contained in *Research Disclosure*, item 308119, Section IV, December, 1989. Additional teachings relating to specific combinations of spectral sensitizing dyes also include U.S. Patent 4,581,329 (Sugimoto et al.), U.S. Patent 4,582,786 (Ikeda et al.), U.S. Patent, U.S. Patent 4,609,621 (Sugimoto et al.), U.S. Patent 4,675,279 (Shuto et al.), U.S. Patent 4,678,741 (Yamada et al.), U.S. Patent 4,720,451 (Shuto et al.), U.S. Patent 4,818,675 (Miyasaka et al.), U.S. Patent 4,945,036 (Arai et al.), and U.S. Patent 4,952,491 (Nishikawa et al.). Additional classes of dyes useful for spectral sensitization, including sensitization at other wavelengths are described in

*Research Disclosure*, 1994, item 36544, section V. All of the above publications and patents are incorporated herein by reference.

Specific examples of useful spectral sensitizing dyes for the photo-thermographic materials of this invention include, for example, 2-[[5-chloro-3-(3-sulfopropyl)-2(3H)-benzothiazolylidene]methyl]-1-(3-sulfopropyl)-naphtho[1,2-d]thiazolium, inner salt, N,N-diethylethanamine salt (1:1), 2-[[5,6-dichloro-1-ethyl-1,3-dihydro-3-(3-sulfopropyl)-2H-benzimidazol-2-ylidene]methyl]-5-phenyl-3-(3-sulfopropyl)-benzoxazolium, inner salt, potassium salt, 5-chloro-2-[[5-chloro-3-(3-sulfopropyl)-2(3H)-benzothiazolylidene]methyl]-3-(3-sulfopropyl)-benzothiazolium, inner salt, N,N-diethylethanamine salt (1:1), and 5-phenyl-2-((5-phenyl-3-(3-sulfopropyl)-2(3H)-benzoxazolylidene)methyl)-3-(3-sulfopropyl)-benzothiazolium, inner salt, N,N-diethylethanamine salt(1:1).

Also useful are spectral sensitizing dyes that decolorize by the action of light or heat. Such dyes are described in U.S. Patent 4,524,128 (Edwards et al.), JP Kokai 2001-109101 (Adachi), JP Kokai 2001-154305 (Kita et al.), and JP 2001-183770 (Hanyu et al.).

Spectral sensitizing dyes may be used singly or in combination. The dyes are selected for the purpose of adjusting the wavelength distribution of the spectral sensitivity, and for the purpose of supersensitization. When using a combination of dyes having a supersensitizing effect, it is possible to attain much higher sensitivity than the sum of sensitivities that can be achieved by using each dye alone. It is also possible to attain such supersensitizing action by the use of a dye having no spectral sensitizing action by itself, or a compound that does not substantially absorb visible light. Diaminostilbene compounds are often used as supersensitizers.

An appropriate amount of spectral sensitizing dye added is generally about  $10^{-10}$  to  $10^{-1}$  mole, and preferably, about  $10^{-7}$  to  $10^{-2}$  mole per mole of silver halide.

### Non-Photosensitive Source of Reducible Silver Ions

The non-photosensitive source of reducible silver ions used in photothermographic materials of this invention can be any organic compound that contains reducible silver(I) ions that does not contain a carboxylate group.

- 5 Preferably, it is a silver salt or coordination complex that is comparatively stable to light and forms a silver image when heated to 50°C or higher in the presence of an exposed silver halide and a reducing agent composition.

Silver salts of nitrogen-containing heterocyclic compounds are preferred, and one or more silver salts of compounds containing an imino group  
10 are particularly preferred. Representative compounds of this type include, but are not limited to, silver salts of benzotriazole and substituted derivatives thereof (for example, silver methylbenzotriazole and silver 5-chlorobenzotriazole), silver salts of 1,2,4-triazoles or 1-*H*-tetrazoles such as phenylmercaptotetrazole as described in U.S. Patent 4,220,709 (deMauriac), and silver salts of imidazole and imidazole  
15 derivatives as described in U.S. Patent 4,260,677 (Winslow et al.). Particularly useful silver salts of this type are the silver salts of benzotriazole, substituted derivatives thereof, or mixtures of two or more of these salts. A silver salt of benzotriazole is most preferred in the photothermographic emulsions and materials of this invention.

20 Silver salts of compounds containing mercapto or thione groups and derivatives thereof can also be used. Preferred compounds of this type include a heterocyclic nucleus containing 5 or 6 atoms in the ring, at least one of which is a nitrogen atom, and other atoms being carbon, oxygen, or sulfur atoms. Such heterocyclic nuclei include, but are not limited to, triazoles, oxazoles, thiazoles, thiazolines, imidazoles, diazoles, pyridines, and triazines. Representative  
25 examples of these silver salts include, but are not limited to, a silver salt of 3-mercapto-4-phenyl-1,2,4-triazole, a silver salt of 2-mercaptobenzimidazole, a silver salt of 2-mercapto-5-aminothiadiazole, a silver salt of 2-(2-ethylglycol-amido)benzothiazole, silver salts of thioglycolic acids (such as a silver salt of a  
30 S-alkylthioglycolic acid, wherein the alkyl group has from 12 to 22 carbon atoms), silver salts of dithiocarboxylic acids (such as a silver salt of dithioacetic acid), a

silver salt of thioamide, a silver salt of 5-carboxylic-1-methyl-2-phenyl-4-thiopyridine, a silver salt of mercaptotriazine, a silver salt of 2-mercaptobenzoxazole, silver salts as described in U.S. Patent 4,123,274 (Knight et al.) (for example, a silver salt of a 1,2,4-mercaptotriazole derivative, such as a silver salt of  
5 3-amino-5-benzylthio-1,2,4-triazole), and a silver salt of thione compounds [such as a silver salt of 3-(2-carboxyethyl)-4-methyl-4-thiazoline-2-thione as described in U.S. Patent 3,785,830 (Sullivan et al.). Examples of other useful silver salts of mercapto or thione substituted compounds that do not contain a heterocyclic nucleus include but are not limited to, a silver salt of thioglycolic acids such as a  
10 silver salt of an S-alkylthioglycolic acid (wherein the alkyl group has from 12 to 22 carbon atoms), a silver salt of a dithiocarboxylic acid such as a silver salt of a dithioacetic acid, and a silver salt of a thioamide.

Silver salts of sulfonates are also useful in the practice of this invention. Such materials are described for example in U.S. Patent 4,504,575  
15 (Lee). Silver salts of sulfosuccinates are also useful as described for example in EP 0 227 141A1 (Leenders et al.).

Non-photosensitive sources of reducible silver ions can also be provided as core-shell silver salts such as those described in U.S. Patent 6,355,408 (Whitcomb et al.), that is incorporated herein by reference. These silver salts  
20 include a core comprised of one or more silver salts and a shell having one or more different silver salts.

Still another source of non-photosensitive reducible silver ions in the practice of this invention are the silver dimer compounds that comprise two different silver salts as described in U.S. Patent 6,566,045 (Whitcomb), that is  
25 incorporated herein by reference. Such non-photosensitive silver dimer compounds comprise two different silver salts, provided that when the two different silver salts comprise straight-chain, saturated hydrocarbon groups as the silver coordinating ligands, those ligands differ by at least 6 carbon atoms.

As one skilled in the art would understand, the non-photosensitive  
30 source of reducible silver ions can include various mixtures of the various silver salt compounds described herein, in any desirable proportions. However, if

mixtures of silver salts are used, it is preferred that at least 50 mol% of the total silver salts be composed of silver salts of compounds containing an imino group as defined above.

5 The photocatalyst and the non-photosensitive source of reducible silver ions must be in catalytic proximity (that is, reactive association). It is preferred that these reactive components be present in the same emulsion layer.

The one or more non-photosensitive sources of reducible silver ions are preferably present in an amount of about 5% by weight to about 70% by weight, and more preferably, about 10% to about 50% by weight, based on the  
10 total dry weight of the emulsion layers. Stated another way, the amount of the sources of reducible silver ions is generally present in an amount of from about 0.001 to about 0.2 mol/m<sup>2</sup> of the dry photothermographic material, and preferably from about 0.01 to about 0.05 mol/m<sup>2</sup> of that material.

The total amount of silver (from all silver sources) in the photo-  
15 thermographic materials is generally at least 0.002 mol/m<sup>2</sup> and preferably from about 0.01 to about 0.05 mol/m<sup>2</sup>.

### **Reducing Agents**

When used in a photothermographic material, the one or more  
20 reducing agents for the source of reducible silver ions can be any ascorbic acid or reductone that can reduce silver(I) ion to metallic silver.

An "ascorbic acid" reducing agent (also referred to as a developer or developing agent) means ascorbic acid, complexes thereof, and derivatives thereof. Ascorbic acid reducing agents are described in a considerable number of  
25 publications in photographic processes, including U.S. Patent 5,236,816 (Purol et al.) and references cited therein.

Useful ascorbic acid reducing agents include ascorbic acid and the analogues, isomers, complexes, and derivatives thereof. Such compounds include, but are not limited to, D- or L-ascorbic acid, 2,3-dihydroxy-2-cyclohexen-1-one,  
30 3,4-dihydroxy-5-phenyl-2(5H)-furanone, sugar-type derivatives thereof (such as sorboascorbic acid,  $\gamma$ -lactoascorbic acid, 6-desoxy-L-ascorbic acid, L-rhamno-

ascorbic acid, imino-6-desoxy-L-ascorbic acid, glucoascorbic acid, fucoascorbic acid, glucoheptoascorbic acid, maltoascorbic acid, L-arabosascorbic acid), sodium ascorbate, niacinamide ascorbate, potassium ascorbate, isoascorbic acid (or L-erythroascorbic acid), and salts thereof (such as alkali metal, ammonium or  
5 others known in the art), endiol type ascorbic acid, an enaminol type ascorbic acid, a thioenol type ascorbic acid, and an enamin-thiol type ascorbic acid, as described for example in U.S. Patent 5,498,511 (Yamashita et al.), EP 0 585 792 A1 (Passarella et al.), EP 0 573 700 A1 (Lingier et al.), EP 0 588 408 A1 (Hieronymus et al.), U.S. Patent 5,089,819 (Knapp), U.S. Patent 5,278,035 (Knapp), U.S. Patent  
10 5,384,232 (Bishop et al.), U.S. Patent 5,376,510 (Parker et al.), JP Kokai 7-56286 (Toyoda), U.S. Patent 2,688,549 (James et al.), and *Research Disclosure*, publication 37152, March 1995. Mixtures of these developing agents can be used if desired.

A "reductone" reducing agent means a class of unsaturated, di- or  
15 poly-enolic organic compounds which, by virtue of the arrangement of the enolic hydroxyl groups with respect to the unsaturated linkages, possess characteristic strong reducing power. The parent compound, "reductone" is 3-hydroxy-2-oxo-propionaldehyde (enol form) and has the structure  $\text{HOCH}=\text{CH}(\text{OH})\text{-CHO}$ . In some reductones, an amino group, a mono-substituted amino group or an imino  
20 group may replace one or more of the enolic hydroxyl groups without affecting the characteristic reducing behavior of the compound.

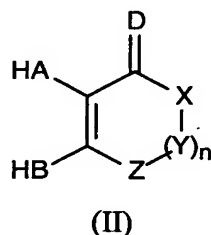
Reductone developing agents are described in a considerable number of publications in photographic processes, including U.S. Patents 2,691,589 (Henn et al), 3,615,440 (Bloom), 3,664,835 (Youngquist et al.),  
25 3,672,896 (Gabrielson et al.), 3,690,872 (Gabrielson et al.), 3,816,137 (Gabrielson et al.), 4,371,603 (Bartels-Keith et al.), 5,712,081 (Andriesen et al.), and U.S. Patent 5,427,905 (Freedman et al.), all of which references are incorporated herein by reference.

Reductone developing agents may be prepared by techniques  
30 known in the art as described in for example, Francis et al., *J. Amer. Chem. Soc.*, **1913**, 2238, Hesse et al., *Annalen*, **1964**, 679, 100, Hesse, *Annalen* **1971**, 747, 84,

Hesse, *Annalen* **1955**, 592, 137, 145, Weygand et al, *Tetrahedron* **1959**, 6, 123, Witiak et al., *J. Org. Chem.*, **1990**, 55, 1112-1114, Dahn et al., *Helv. Chim. Acta*. **1954**, 54, 1318-1327, Eistert et al. *Chem. Ber.* **1960**, 93, 1451, Weber et al., *Annalen* **1972**, 763, 66, and Cavill et al., *J. Chem. Soc. (London)*, **1955**, 4426.

- 5                      Reductone reducing agents include: 1,3-di-*p*-tolyl-2,3-dihydroxy-2-propene-1-one, 1,3-dipyridyl-2,3-dihydroxy-2-propene-1-one, 1-phenyl-3-pyridyl-2,3-dihydroxy-2-propene-1-one, 1,3-dithienyl-2,3-dihydroxy-2-propene-1-one, 1-phenyl-3-furyl-2,3-dihydroxy-2-propene-1-one, 1,3-dibenzyl-2,3-dihydroxy-2-propene-1-one, 1,3-dibutyl-2,3-dihydroxy-2-propene-1-one,
- 10    1-propyl-3-cyclohexyl-2,3-dihydroxy-2-propene-1-one, 1-propyl-3-(*o*-methoxyphenyl)-2,3-dihydroxy-2-propene-1-one, 1-(*p*-chloropyridyl)-3-(2-methoxyethyl)-2,3-dihydroxy-2-propene-1-one, 4,5-dimethyl reductic acid, 4,4-dimethyl-reductic acid, 4-methoxy-reductic acid, 4,5-diethyl-reductic acid, 4,5-di(chloromethyl)-reductic acid, 4-propyl-reductic acid, 4,6-dimethyl-2,3-dihydroxy-cyclohex-
- 15    2-ene-1-one, 5,5-dimethyl-2,3-dihydroxy-cyclohex-2-ene-1-one, 5-bromo-2,3-dihydroxy-cyclohex-2-ene-1-one, 5-bromo-4,6-dimethyl-2,3-dihydroxy-cyclohex-2-ene-1-one, 5-ethyl-2,3-dihydroxy-cyclohex-2-ene-1-one, 5,5-dimethoxy-2,3-dihydroxy-cyclohex-2-ene-1-one, 5-thioethyl-2,3-dihydroxy-cyclohex-2-ene-1-one, 2,3-dihydroxy-cyclohept-2-ene-1-one, 5-methyl-
- 20    2,3-dihydroxy-cyclohept-2-ene-1-one, 5-methyl-2,3-dihydroxy-cyclohept-2-ene-1-one, 2,3-dihydroxy-cyclobut-2-ene-1-one, 4-butyl-2,3-dihydroxy-cyclobut-2-ene-1-one, and 4,4-dimethyl-2,3-dihydroxy-cyclobut-2-ene-1-one.

- In some embodiments, the ascorbic acid compound or reductone
- 25    compound is represented by Structure (II):

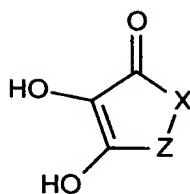


wherein A, B, and D each independently represents O or NR<sub>7</sub>, X represents O, NR<sub>8</sub>, CR<sub>9</sub>R<sub>10</sub>, C=O, or C=NR<sub>11</sub>, Y represents O, NR'<sub>8</sub>, CR'<sub>9</sub>R'<sub>10</sub>, C=O, or C=NR'<sub>11</sub>, Z represents O, NR''<sub>8</sub>, CR''<sub>9</sub>R''<sub>10</sub>, C=O, or CNR''<sub>11</sub>, and n is 0 or 1.

Moreover, in Structure (II) above, R<sub>7</sub>, R<sub>8</sub>, R<sub>9</sub>, R<sub>10</sub> and R<sub>11</sub>, R'<sub>7</sub>, R'<sub>8</sub>, R'<sub>9</sub>, R'<sub>10</sub>, and R'<sub>11</sub>, and R''<sub>7</sub>, R''<sub>8</sub>, R''<sub>9</sub>, R''<sub>10</sub>, and R''<sub>11</sub>, each independently represents hydrogen, an alkyl group (preferably having from 1 to 18 carbon atoms), an aralkyl group (preferably having from 7 to 15 carbon atoms), an alkenyl group (preferably having from 2 to 5 carbon atoms), an alkynyl group (preferably having from 2 to 5 carbon atoms), a cycloalkyl or cycloalkenyl group (preferably having 3 to 7 carbon atoms forming the ring), an aryl group (preferably having 6 to 10 carbon atoms forming one or more aromatic rings), or an aromatic or non-aromatic heterocyclyl group (preferably having 5 or 6 carbon, nitrogen, oxygen, and sulfur atoms forming the aromatic or non-aromatic ring), or R<sub>9</sub> and R<sub>10</sub>, R'<sub>9</sub> and R'<sub>10</sub>, or R''<sub>9</sub> and R''<sub>10</sub>, may further represent the number of atoms necessary to form a saturated or unsaturated carbocyclic or heterocyclic ring (preferably having 5 to 7 atoms within the ring), wherein when X is CR<sub>9</sub>R<sub>10</sub> and Y is CR'<sub>9</sub>R'<sub>10</sub>, R<sub>9</sub> and R'<sub>9</sub> and/or R<sub>10</sub> and R'<sub>10</sub> may represent the number of atoms necessary to form a saturated or unsaturated carbocyclic or heterocyclic ring (preferably having 5 to 7 atoms within the ring), and wherein when Y is CR'<sub>9</sub>R'<sub>10</sub> and Z is CR''<sub>9</sub>R''<sub>10</sub> and n=1, then R'<sub>9</sub> and R''<sub>9</sub> and/or R'<sub>10</sub> and R''<sub>10</sub> may represent the number of atoms necessary to form a saturated or unsaturated carbocyclic or heterocyclic ring (preferably having 5 to 7 atoms within the ring). All of the noted groups defined in this paragraph can be substituted with one or more substituents that would be readily apparent to a skilled worker in the art. It would also be apparent to a skilled worker in the art that some combinations of X, Y, and Z as defined above are not chemically possible. Thus, a skilled worker would be able to design compounds of Structure II with suitable X, Y, and Z groups that are chemically possible and useful in the practice of the present invention.

In one preferred embodiment, the reducing agent is an ascorbic acid compound or reductone compound represented by Structure (IIa):



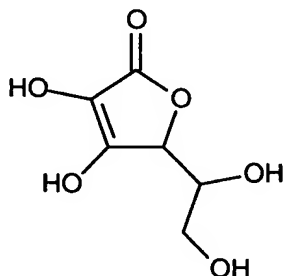


(IIa)

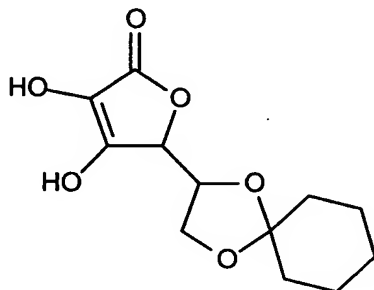
wherein X represents an O, NR<sub>8</sub>, or CR<sub>9</sub>R<sub>10</sub> group and Z represents CR<sup>"</sup><sub>9</sub> R<sup>"</sup><sub>10</sub>  
 5 wherein R<sub>9</sub> is hydrogen and R<sub>10</sub> is a substituted or unsubstituted alkyl group  
 having from 1 to 6 carbon atoms or a substituted or unsubstituted aryl group.

In a more preferred embodiment, X is O and Z represents CR<sup>"</sup><sub>9</sub>  
 R<sup>"</sup><sub>10</sub> wherein R<sub>9</sub> is hydrogen and R<sub>10</sub> is a substituted or unsubstituted alkyl group  
 having from 1 to 6 carbon atoms or a substituted or unsubstituted phenyl group.

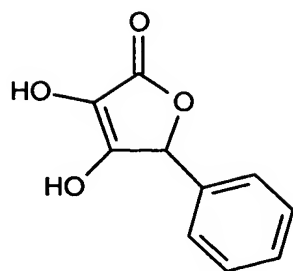
10 Representative ascorbic acid or reductone reducing agent  
 compounds having Structure (II) useful in the practice of the present invention  
 include the following Compounds RA-1 to RA-26:



(RA-1)

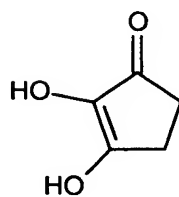


(RA-2)



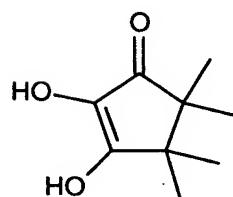
(RA-3)

5



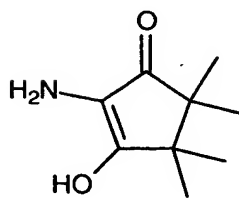
(RA-4)

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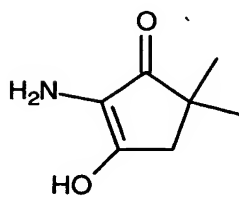


(RA-5)

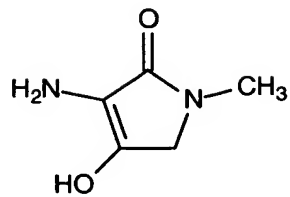
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(RA-6)

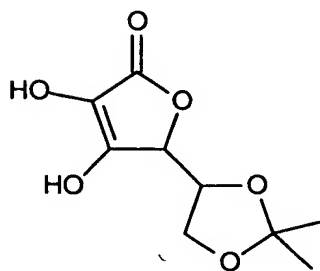


(RA-7)



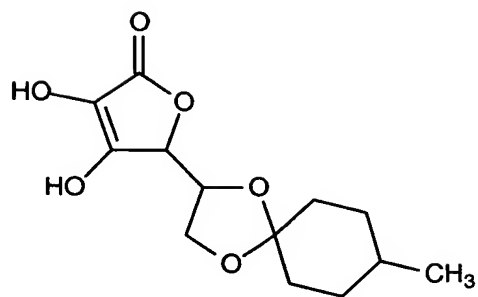
(RA-8)

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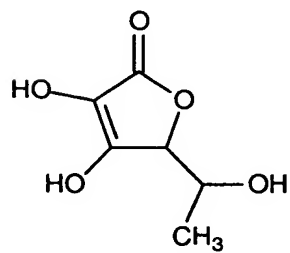
(RA-9)

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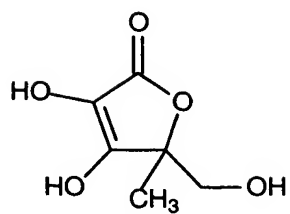


(RA-10)

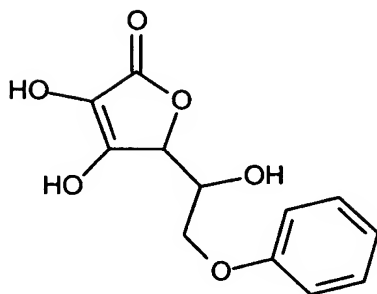
15



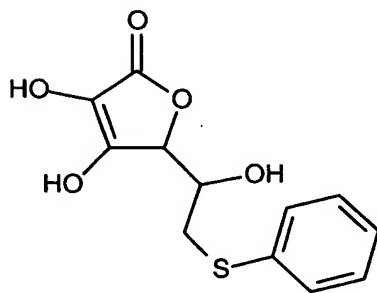
(RA-11)



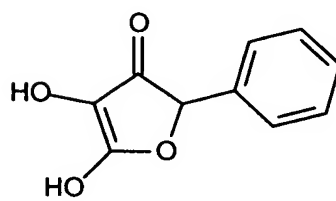
(RA-12)



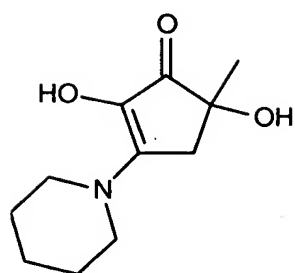
(RA-13)



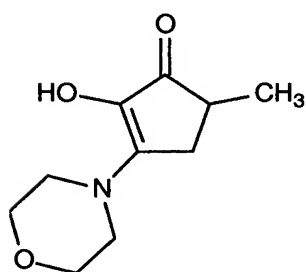
(RA-14)



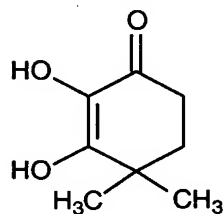
(RA-15)



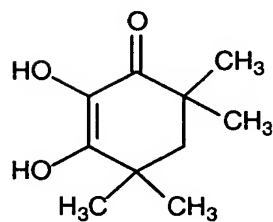
(RA-16)



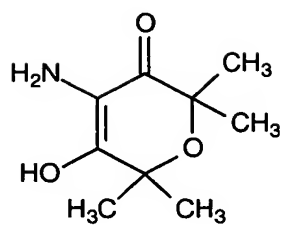
(RA-17)



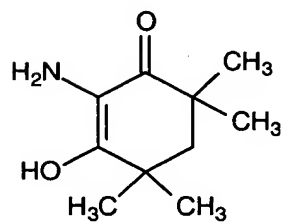
(RA-18)



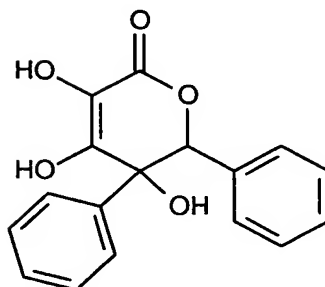
(RA-19)



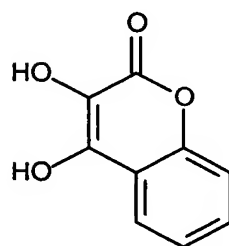
(RA-20)



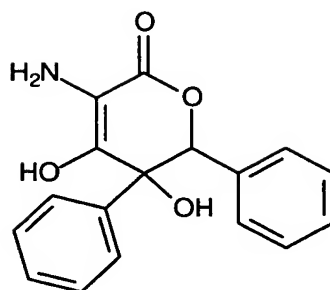
(RA-21)



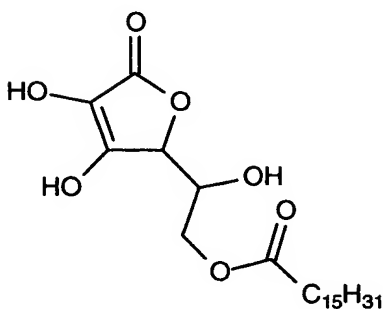
(RA-22)



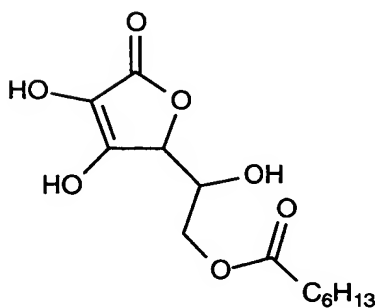
(RA-23)



(RA-24)



(RA-25)



(RA-26).

Ascorbic acid reducing agents are preferred, particularly when a silver salt of a compound containing an imino group (such as, for example, a silver benzotriazole) is used as the source of reducible silver ions. Ascorbic acid and 3,4-dihydroxy-5-phenyl-2(5H)-furanone are specifically preferred in such embodiments.

If desired, co-developers and contrast enhancing agents may be used in combination with the ascorbic acid and reductone reducing agents described herein.

Useful co-developer reducing agents include for example, those  
5 described in U.S. Patent 6,387,605 (Lynch et al.) that is incorporated herein by reference. Examples of these compounds include, but are not limited to, 2,5-dioxo-cyclopentane carboxaldehydes, 5-(hydroxymethylene)-2,2-dimethyl-1,3-dioxane-4,6-diones, 5-(hydroxymethylene)-1,3-dialkylbarbituric acids, and 2-(ethoxymethylene)-1H-indene-1,3(2H)-diones.

10 Additional classes of reducing agents that may be used as co-developers are trityl hydrazides and formyl phenyl hydrazides as described in U.S. Patent 5,496,695 (Simpson et al.), 2-substituted malondialdehyde compounds as described in U.S. Patent 5,654,130 (Murray), and 4-substituted isoxazole compounds as described in U.S. Patent 5,705,324 (Murray). Additional  
15 developers are described in U.S. Patent 6,100,022 (Inoue et al.). All of the patents above are incorporated herein by reference.

Yet another class of co-developers includes substituted acrylonitrile compounds that are described in U.S. Patent 5,635,339 (Murray) and U.S. Patent 5,545,515 (Murray et al.), both incorporated herein by reference. Examples of  
20 such compounds include, but are not limited to, the compounds identified as HET-01 and HET-02 in U.S. Patent 5,635,339 (noted above) and CN-01 through CN-13 in U.S. Patent 5,545,515 (noted above). Particularly useful compounds of this type are (hydroxymethylene)cyanoacetates and their metal salts.

Various contrast enhancing agents may be used in some photo-  
25 thermographic materials with specific co-developers. Examples of useful contrast enhancing agents include, but are not limited to, hydroxylamines (including hydroxylamine and alkyl- and aryl-substituted derivatives thereof), alkanolamines and ammonium phthalamate compounds as described for example, in U.S. Patent 5,545,505 (Simpson), hydroxamic acid compounds as described for example, in  
30 U.S. Patent 5,545,507 (Simpson et al.), N-acylhydrazine compounds as described for example, in U.S. Patent 5,558,983 (Simpson et al.), and hydrogen atom donor



compounds as described in U.S. Patent 5,637,449 (Harring et al.). All of the patents above are incorporated herein by reference.

The reducing agent (or mixture thereof) described herein is generally present as 1 to 10% (dry weight) of the emulsion layer. In multilayer constructions, if the reducing agent is added to a layer other than an emulsion layer, slightly higher proportions, of from about 2 to 15 weight % may be more desirable. Any co-developers may be present generally in an amount of from about 0.001% to about 1.5% (dry weight) of the emulsion layer coating.

## 10 Polycarboxylic Acid Compounds

It is essential that the photothermographic materials of this invention include in the one or more imaging layers a polycarboxylic acid that has a pKa of less than 4.5. It is more preferred that the polycarboxylic acid have a pKa of less than 4. Mixtures of such polycarboxylic acids can be provided in one or more of such layers.

It is preferred that the photothermographic materials of this invention include one or more polycarboxylic acid compounds that are represented by the following Structure (I):



wherein Q represents a direct bond, a phenylene linking group, or a substituted or unsubstituted aliphatic linking group consisting of 1 or 2 carbon atoms.

25 In Structure (I), each carbon atom in the phenylene group can be further substituted.

In Structure (I), when Q represents an aliphatic group consisting of 1 or 2 carbons, Q can be substituted with one or more carboxy groups ( -COOH ), alkylcarboxy groups having 1 to 6 carbon atoms in the alkyl moiety [such as methylcarboxy ( -COOCH<sub>3</sub> )], hydroxy groups, carboxyalkyl groups having 1 to 3 carbon atoms in the alkyl moiety [such as carboxymethyl ( -CH<sub>2</sub>COOH ) or carboxyethyl ( -CH<sub>2</sub>CH<sub>2</sub>COOH ) ], alkyl groups having 1 to 4 carbon atoms such

as methyl, ethyl *iso*-propyl, *n*-butyl, and *t*-butyl) or two alkyl groups on the same carbon may be connected to form a 3- to 6-membered cycloalkyl ring (such as cyclopropyl or cyclobutyl), alkenyl groups having 2 to 4 carbon atoms (such as vinyl, allyl and propenyl), 5- to 6-membered cycloalkyl (such as cyclopentyl or cyclohexyl), phenyl groups, aralkyl groups (such as benzyl), or non-basic  
5 heterocyclic groups (such as thienyl and furanyl). All of these substituents can be further substituted, as one skilled in the art would readily appreciate.

In some preferred embodiments, Q represents a substituted or unsubstituted aliphatic chain consisting of 2 carbon atoms in the chain (such as an  
10 ethylene group). In more preferred embodiments, at least one of those two carbon atoms is substituted with a hydroxy, carboxy, or carboxyalkyl group as defined above. In such more preferred embodiments, Q is particularly -CH<sub>2</sub>-C(OH)(CH<sub>2</sub>COOH)-.

Representative compounds having Structure (I) that are useful as  
15 stabilizers in the practice of this invention include but are not limited to the following listed compounds (and mixtures thereof):

3-thiophenemalonic acid, allylmalonic acid, benzylmalonic acid, 1,2,3,4-butanetetracarboxylic acid, 3-butene-1,2,3-tricarboxylic acid, butyl malonic acid, D-(-)-citramalic acid, L-(+)-citramalic acid, citric acid,  
20 1,1-cyclobutanedicarboxylic acid, 1,1-cyclopropanedicarboxylic acid, dihydroxymalonic acid, dimethylmalonic acid, 1,1,2-ethanetricarboxylic acid, hemimellitic acid, homoisocitric acid, hydroxycitric acid, 2-hydroxy-2-isopropylsuccinic acid, 1-indanylmalonic acid, isocitric acid, ketomalonic acid monohydrate, D-malic acid, L-malic acid, D,L-malic acid, malonic acid, meso-tartaric acid, meso-tartaric acid monohydrate, D,L-2-methylcitric acid, methylmalonic acid, 2-methylpropane-  
25 tricarboxylic acid, D,L-methyltartronic acid, oxalic acid, phenylmalonic acid, phthalic acid, succinic acid, D-(-)-tartaric acid, L-(+)-tartaric acid, D,L-tartaric acid, D,L-tartaric acid hydrate, tartronic acid, D,L-threo-3-isopropylmalic acid, and tricarballic acid.

Citric acid, tricarballic acid, 1,2,3,4-butanetetracarboxylic acid, tartaric acid, succinic acid, phthalic acid, hemimellitic acid, oxalic acid, malonic acid, malic acid, butyl malonic acid, and mixtures thereof, are preferred.

Citric acid, tricarballic acid, phthalic acid, 1,2,3,4-butanetetracarboxylic acid, tartaric acid, and mixtures thereof, are particularly preferred.  
Citric acid, tricarballic acid, and mixtures thereof are most preferred.

These compounds are available from commercial sources or can be prepared by methods known in the art.

The one or more polycarboxylic acids are present in an amount of from about 0.05 to about 1 mol/mol of silver halide and preferably in an amount of from about 0.25 to about 0.5 mol/mol of silver halide.

To maintain the acidity of the imaging layer, or of the protective overcoat layer, the photothermographic materials of this invention are substantially free of compounds that form or release a basic material upon coating, drying, storage, or development.

It is preferred that the surface pH of the outermost one or more imaging layers, or of the protective topcoat layer if present, be less than 7 and more than 3. It is more preferred that this surface pH be from about 3 to about 5.5. It is most preferred that this surface pH be from about 4.5 to about 5.5. The surface pH can be determined using a surface pH electrode after placing a drop of potassium nitrate ( $\text{KNO}_3$ ) solution on the surface of the coated layer being evaluated. Such electrodes are available from Corning Incorporated (Corning, NY).

## **25    Toners**

The thermally developable materials of this invention can also include one or more compounds that are known in the art as “toners.” Toners are compounds that when added to the photothermographic imaging layer shift the color of the developed silver image from yellowish-orange to brown-black or blue-black, and/or act as development accelerators to speed up thermal development. They also increase the optical density of the developed image.

Without them, images are often faint and yellow or brown. The use of “toners” or derivatives thereof that improve the black-and-white image are highly desirable components of the photothermographic materials of this invention.

Thus, the thermally developable materials of this invention can also  
5 include one or more compounds that either act as toners or react with a reducing agent to provide toners in an amount of about 0.01% by weight to about 10%, and more preferably about 0.1% by weight to about 10% by weight, based on the total dry weight of the layer in which they are included. The amount can also be defined as being within the range of from about  $1 \times 10^{-5}$  to about 1.0 mol per mole  
10 of non-photosensitive source of reducible silver in the photothermographic material. The toner compounds may be incorporated in one or more of the thermally developable layers as well as in adjacent layers such as a protective overcoat layer or underlying “carrier” layer. Toners can be located on both sides of the support if thermally developable layers are present on both sides of the  
15 support.

Compounds useful as toners are described, for example, in U.S. Patent 3,080,254 (Grant, Jr.), U.S. Patent 3,847,612 (Winslow), U.S. Patent 4,123,282 (Winslow), U.S. Patent 4,082,901 (Laridon et al.), U.S. Patent 3,074,809 (Owen), U.S. Patent 3,446,648 (Workman), U.S. Patent 3,844,797  
20 (Willems et al.), U.S. Patent 3,951,660 (Hagemann et al.), U.S. Patent 5,599,647 (Defieuw et al.) and GB 1,439,478 (AGFA).

Additional useful toners are substituted and unsubstituted mercaptotriazoles as described for example in U.S. Patent 3,832,186 (Masuda et al.), U.S. Patent 6,165,704 (Miyake et al.), U.S. Patent 5,149,620 (Simpson et al.),  
25 copending and commonly assigned U.S. Serial No. 10/193,443 (filed July 11, 2002 by Lynch, Zou, and Ulrich) and U.S. Serial No. 10/192,944 (filed July 11, 2002 by Lynch, Ulrich, and Zou), as well as the triazine thione compounds described in U.S. Serial No. 10/341,754 (filed January 14, 2003 by Lynch, Ulrich, and Skoug), and the heterocyclic disulfide compounds described in U.S. Serial No.  
30 10/384,244 (filed March 7, 2003 by Lynch and Ulrich), all of which are incorporated herein by reference.

Phthalazine and phthalazine derivatives [such as those described in U.S. Patent 6,146,822 (Asanuma et al.) incorporated herein by reference], as well as phthalazinone, and phthalazinone derivatives are particularly useful toners.

Particularly useful are the phthalazine compounds described in  
5 commonly assigned U.S. Patent 6,605,418 (Ramsden et al.) incorporated herein by reference. These materials are believed to be particularly effective in accelerating image development.

Examples of toners include, but are not limited to, phthalimide and  
10 *N*-hydroxyphthalimide, cyclic imides (such as succinimide), pyrazoline-5-ones, quinazolinone, 1-phenylurazole, 3-phenyl-2-pyrazoline-5-one, and 2,4-thiazolidinedione, naphthalimides (such as *N*-hydroxy-1,8-naphthalimide), cobalt complexes [such as hexaamminecobalt(3+) trifluoroacetate], mercaptans (such as 3-mercapto-1,2,4-triazole, 2,4-dimercaptopyrimidine, 3-mercapto-4-benzyl-1,2,4-triazole, 3-mercapto-4-phenyl-1,2,4-triazole, 3-mercapto-  
15 4,5-diphenyl-1,2,4-triazole and 2,5-dimercapto-1,3,4-thiadiazole), *N*-(amino-methyl)aryldicarboximides (such as (N,N-dimethylaminomethyl)phthalimide), and N-(dimethylaminomethyl)naphthalene-2,3-dicarboximide, a combination of blocked pyrazoles, isothiuronium derivatives, merocyanine dyes {such as 3-ethyl-5-[(3-ethyl-2-benzothiazolinyldiene)-1-methyl-ethylidene]-2-thio-2,4-*o*-azolidine-  
20 dione}, phthalazine and derivatives thereof [such as those described in U.S. Patent 6,146,822 (Asanuma et al., noted above)], phthalazinone and phthalazinone derivatives, or metal salts or these derivatives [such as 4-(1-naphthyl)-phthalazinone, 6-chlorophthalazinone, 5,7-dimethoxyphthalazinone, and 2,3-dihydro-1,4-phthalazinedione], a combination of phthalazine (or derivative  
25 thereof) plus one or more phthalic acid derivatives (such as phthalic acid, 4-methylphthalic acid, 4-nitrophthalic acid, and tetrachlorophthalic anhydride), quinazolinediones, benzoxazine or naphthoxazine derivatives, rhodium complexes functioning not only as tone modifiers but also as sources of halide ion for silver halide formation *in situ* [such as ammonium hexachlororhodate (3+), rhodium  
30 bromide, rhodium nitrate, and potassium hexachlororhodate (3+)], benzoxazine-2,4-diones (such as 1,3-benzoxazine-2,4-dione, 8-methyl-1,3-benzoxazine-

2,4-dione and 6-nitro-1,3-benzoxazine-2,4-dione), pyrimidines and asym-triazines (such as 2,4-dihydroxypyrimidine, 2-hydroxy-4-aminopyrimidine and azauracil) and tetraazapentalene derivatives [such as 3,6-dimercapto-1,4-diphenyl-*1H,4H*-2,3a,5,6a-tetraazapentalene and 1,4-di-(*o*-chlorophenyl)-3,6-dimercapto-*1H,4H*-2,3a,5,6a-tetraazapentalene].

### Other Addenda

The photothermographic materials of this invention can also contain other additives such as shelf-life stabilizers, antifoggants, contrast enhancing agents, development accelerators, acutance dyes, post-processing stabilizers or stabilizer precursors, thermal solvents (also known as melt formers), humectants, and other image-modifying agents as would be readily apparent to one skilled in the art.

To further control the properties of photothermographic materials, (for example, contrast,  $D_{\min}$ , speed, or fog), it may be preferable to add one or more heteroaromatic mercapto compounds or heteroaromatic disulfide compounds of the formulae  $\text{Ar-S-M}^1$  and  $\text{Ar-S-S-Ar}$ , wherein  $\text{M}^1$  represents a hydrogen atom or an alkali metal atom and Ar represents a heteroaromatic ring or fused heteroaromatic ring containing one or more of nitrogen, sulfur, oxygen, selenium, or tellurium atoms. Preferably, the heteroaromatic ring comprises benzimidazole, naphthimidazole, benzothiazole, naphthothiazole, benzoxazole, naphthoxazole, benzoselenazole, benzotellurazole, imidazole, oxazole, pyrazole, triazole, thiazole, thiadiazole, tetrazole, triazine, pyrimidine, pyridazine, pyrazine, pyridine, purine, quinoline, or quinazolinone. Compounds having other heteroaromatic rings and compounds providing enhanced sensitization at other wavelengths are also envisioned to be suitable. For example, heteroaromatic mercapto compounds are described as supersensitizers for infrared photothermographic materials in EP 0 559 228 B1 (Philip Jr. et al.). These compounds are useful as addenda when added to the emulsion along with the sensitizing dye (where they are especially beneficial with red and infrared sensitive films), and especially when used in organic [for example, poly(vinyl butyral)] or aqueous latex binders.

The photothermographic materials of the present invention can be further protected against the production of fog and can be stabilized against loss of sensitivity during storage. While not necessary for the practice of the invention, it may be advantageous to add mercury(II) salts to the emulsion layer(s) as an  
5 antifoggant. Preferred mercury(II) salts for this purpose are mercuric acetate and mercuric bromide. Other useful mercury salts include those described in U.S. Patent 2,728,663 (Allen).

Other suitable antifoggants and stabilizers that can be used alone or in combination include thiazolium salts as described in U.S. Patent 2,131,038  
10 (Brooker et al.) and U.S. Patent 2,694,716 (Allen), azaindenes as described in U.S. Patent 2,886,437 (Piper), triazaindolizines as described in U.S. Patent 2,444,605 (Heimbach), the urazoles described in U.S. Patent 3,287,135 (Anderson), sulfocatechols as described in U.S. Patent 3,235,652 (Kennard), the oximes described in GB 623,448 (Carrol et al.), polyvalent metal salts as described in U.S.  
15 Patent 2,839,405 (Jones), thiuronium salts as described in U.S. Patent 3,220,839 (Herz), palladium, platinum, and gold salts as described in U.S. Patent 2,566,263 (Tirelli) and U.S. Patent 2,597,915 (Damshroder), compounds having -SO<sub>2</sub>CB<sub>3</sub> groups as described for example in U.S. Patent 5,594,143 (Kirk et al.) and U.S. Patent 5,374,514 (Kirk et al.), and 2-(tribromomethylsulfonyl)quinoline  
20 compounds as described in U.S. Patent 5,460,938 (Kirk et al.).

Stabilizer precursor compounds capable of releasing stabilizers upon application of heat during development can also be used. Such precursor compounds are described in for example, U.S. Patent 5,158,866 (Simpson et al.), U.S. Patent 5,175,081 (Krepeski et al.), U.S. Patent 5,298,390 (Sakizadeh et al.),  
25 and U.S. Patent 5,300,420 (Kenney et al.).

In addition, certain substituted-sulfonyl derivatives of benzo-triazoles (for example alkylsulfonylbenzotriazoles and arylsulfonylbenzotriazoles) have been found to be useful stabilizing compounds (such as for post-processing print stabilizing), as described in U.S. Patent 6,171,767 (Kong et al.).

Furthermore, other specific useful antifoggants/stabilizers are described in more detail in U.S. Patent 6,083,681 (Lynch et al.), incorporated herein by reference.

5 The photothermographic materials may also include one or more polyhalo antifoggants that include one or more polyhalo substituents including but not limited to, dichloro, dibromo, trichloro, and tribromo groups. The antifoggants can be aliphatic, alicyclic or aromatic compounds, including aromatic heterocyclic and carbocyclic compounds.

10 Particularly useful antifoggants of this type are polyhalo antifoggants, such as those having a  $-SO_2C(X')_3$  group wherein  $X'$  represents the same or different halogen atoms.

Another class of useful antifoggants includes those compounds described in U.S. Patent 6,514,678 (Burgmaier et al.), incorporated herein by reference.

15 Advantageously, the photothermographic materials of this invention also include one or more thermal solvents (also called “heat solvents,” “thermosolvents,” “melt formers,” “melt modifiers,” “eutectic formers,” “development modifiers,” “waxes,” or “plasticizers”) for improving the reaction speed of the silver-developing redox reaction at elevated temperature.

20 By the term “thermal solvent” in this invention is meant an organic material which becomes a plasticizer or liquid solvent for at least one of the imaging layers upon heating at a temperature above 60°C. Useful for that purpose are polyethylene glycols having a mean molecular weight in the range of 1,500 to 20,000 described in U.S. Patent 3,347,675. Further are mentioned compounds  
25 such as urea, methyl sulfonamide and ethylene carbonate being thermal solvents described in U.S. Patent 3,667,959, and compounds such as tetrahydro-thiophene-1,1-dioxide, methyl anisate and 1,10-decanediol being described as thermal solvents in *Research Disclosure*, December 1976, item 15027, pp. 26-28. Other representative examples of such compounds include, but are not limited to,  
30 niacinamide, hydantoin, 5,5-dimethylhydantoin, salicylanilide, phthalimide, N-hydroxyphthalimide, N-potassium-phthalimide, succinimide, N-hydroxy-



1,8-naphthalimide, phthalazine, 1-(2H)-phthalazinone, 2-acetylphthalazinone, benzanilide, 1,3-dimethylurea, 1,3-diethylurea, 1,3-diallylurea, *meso*-erythritol, D-sorbitol, tetrahydro-2-pyrimidone, glycouril, 2-imidazolidone, 2-imidazolidone-4-carboxylic acid, and benzenesulfonamide. Combinations of these compounds  
5 can also be used including, for example, a combination of succinimide and 1,3-dimethylurea. Known thermal solvents are disclosed, for example, in U.S. Patent 6,013,420 (Windender), U.S. Patent 3,438,776 (Yudelson), U.S. Patent 5,368,979 (Freedman et al.), U.S. Patent 5,716,772 (Taguchi et al.), U.S. Patent 5,250,386 (Aono et al.), and in *Research Disclosure*, December 1976, item 15022.

10

### Phosphors

In some embodiments, it is also effective to incorporate X-radiation-sensitive phosphors in the chemically sensitized photothermographic emulsions and materials described herein. Aqueous-based emulsions and  
15 materials are described in U.S. Patent 6,573,033 (Simpson et al.), organic solvent-based emulsions and materials are described in U.S. Patent 6,440,649 (Simpson et al.), both of which are incorporated herein by reference.

Phosphors are materials that emit infrared, visible, or ultraviolet radiation upon excitation. An intrinsic phosphor is a material that is naturally (that  
20 is, intrinsically) phosphorescent. An “activated” phosphor is one composed of a basic material that may or may not be an intrinsic phosphor, to which one or more dopant(s) has been intentionally added. These dopants “activate” the phosphor and cause it to emit infrared, visible, or ultraviolet radiation. For example, in  $\text{Gd}_2\text{O}_2\text{S:Tb}$ , the Tb atoms (the dopant/activator) give rise to the optical emission  
25 of the phosphor.

Any conventional or useful phosphor can be used, singly or in mixtures, in the practice of this invention.

Storage phosphors can also be used in the practice of this invention. Various storage phosphors are described for example, in U.S. Patent 5,464,568  
30 (noted above), incorporated herein by reference. In these materials, the dopants are involved in the storage as well as the emission of radiation. When storage

phosphors are incorporated within the photothermographic materials, the initial exposure to X-radiation is “stored” within the phosphor particles. When the material is then later exposed a second time to stimulating electromagnetic radiation (usually to visible light or infrared radiation), the “stored” energy is then released as an emission of visible or infrared radiation. The photothermographic materials may then be developed by heating. BaFBr described herein is such a storage phosphor.

The one or more phosphors used in the practice of this invention are present in the photothermographic materials in an amount of at least 0.1 mole per mole, and preferably from about 0.5 to about 20 mole, per mole of total silver in the photothermographic material. Generally, the amount of total silver is at least  $0.002 \text{ mol/m}^2$ .

Because of the size of the phosphors used in the invention, generally the layers in which they are incorporated (usually one or more emulsion layers), have a dry coating weight of at least  $5 \text{ g/m}^2$ , and preferably from about  $5 \text{ g/m}^2$ , to about  $200 \text{ g/m}^2$ . Most preferably, the one or more phosphors and the photosensitive silver halide are incorporated within the same imaging layer that has a dry coating weight within the noted preferred range.

## **20 Binders**

The photocatalyst (such as photosensitive silver halide), the non-photosensitive source of reducible silver ions, the reducing agent composition, antifoggant(s), toner(s), and any other additives used in the present invention are added to and coated in one or more hydrophilic binders. Thus, aqueous-based formulations are used to prepare the photothermographic materials of this invention. Mixtures of different types of hydrophilic binders can also be used.

Examples of useful hydrophilic binders include, but are not limited to, proteins and protein derivatives, gelatin and gelatin derivatives (hardened or unhardened, including alkali- and acid-treated gelatins, and deionized gelatin), cellulosic materials such as hydroxymethyl cellulose and cellulosic esters,

acrylamide/methacrylamide polymers, acrylic/methacrylic polymers, polyvinyl pyrrolidones, polyvinyl alcohols, poly(vinyl lactams), polymers of sulfoalkyl acrylate or methacrylates, hydrolyzed polyvinyl acetates, polyamides, polysaccharides (such as dextrans and starch ethers), and other naturally occurring  
5 or synthetic vehicles commonly known for use in aqueous-based photographic emulsions (see for example *Research Disclosure*, item 38957, noted above). Cationic starches can also be used as peptizers for emulsions containing tabular grain silver halides as described in U.S. Patent 5,620,840 (Maskasky) and U.S. Patent 5,667,955 (Maskasky). Water-dispersible latexes can also be used as the  
10 sole binders or in mixtures with other hydrophobic or hydrophilic binders.

Particularly useful hydrophilic binders are gelatin, gelatin derivatives, polyvinyl alcohols, and cellulosic materials. Gelatin and its derivatives are most preferred, and comprise at least 75 weight % of total binders when a mixture of binders is used.

15 “Minor” amounts of hydrophobic binders can also be present as long as more than 50% (by weight of total binders) is composed of hydrophilic binders. Examples of typical hydrophobic binders include, but are not limited to, polyvinyl acetals, polyvinyl chloride, polyvinyl acetate, cellulose acetate, cellulose acetate butyrate, polyolefins, polyesters, polystyrenes, polyacrylonitrile,  
20 polycarbonates, methacrylate copolymers, maleic anhydride ester copolymers, butadiene-styrene copolymers, and other materials readily apparent to one skilled in the art. Copolymers (including terpolymers) are also included in the definition of polymers. The polyvinyl acetals (such as polyvinyl butyral and polyvinyl formal) and vinyl copolymers (such as polyvinyl acetate and polyvinyl chloride)  
25 are particularly preferred. Particularly suitable binders are polyvinyl butyral resins that are available as BUTVAR<sup>®</sup> B79 (Solutia, Inc.) and PIOLOFORM<sup>®</sup> BS-18 or PIOLOFORM<sup>®</sup> BL-16 (Wacker Chemical Company). Aqueous dispersions (or latexes) of hydrophobic binders may also be used.

30 Hardeners for various binders may be present if desired. Useful hardeners are well known and include vinyl sulfone compounds as described in U.S. Patent 6,143,487 (Philip et al.) and aldehydes and various other hardeners as

described in U.S. Patent 6,190,822 (Dickerson et al.). The hydrophilic binders used in the photothermographic materials are generally partially or fully hardened using any conventional hardener. Useful hardeners are well known and are described, for example, in T. H. James, *The Theory of the Photographic Process*,  
5 Fourth Edition, Eastman Kodak Company, Rochester, NY, 1977, Chapter 2, pp. 77-78.

Where the proportions and activities of the photothermographic materials require a particular developing time and temperature, the binder(s) should be able to withstand those conditions. Generally, it is preferred that the  
10 binder does not decompose or lose its structural integrity at 120°C for 60 seconds. It is more preferred that it does not decompose or lose its structural integrity at 177°C for 60 seconds.

The polymer binder(s) is used in an amount sufficient to carry the components dispersed therein. An effective range of binder amounts can be  
15 readily determined by one skilled in the art. Preferably, a binder is used at a level of about 10% by weight to about 90% by weight, and more preferably at a level of about 20% by weight to about 70% by weight, based on the total dry weight of the layer in which it is included. The amount of binders in double-sided photothermo-  
graphic materials may be the same or different.

20

### **Support Materials**

The photothermographic materials of this invention comprise a polymeric support that is preferably a flexible, transparent film that has any desired thickness and is composed of one or more polymeric materials, depending  
25 upon their use. The supports are generally transparent (especially if the material is used as a photomask) or at least translucent, but in some instances, opaque supports may be useful. They are required to exhibit dimensional stability during thermal development and to have suitable adhesive properties with overlying layers. Useful polymeric materials for making such supports include, but are not  
30 limited to, polyesters (such as polyethylene terephthalate and polyethylene naphthalate), cellulose acetate and other cellulose esters, polyvinyl acetal,

polyolefins (such as polyethylene and polypropylene), polycarbonates, and polystyrenes (and polymers of styrene derivatives). Preferred supports are composed of polymers having good heat stability, such as polyesters and polycarbonates. Polyethylene terephthalate film is a particularly preferred support.

5 Various support materials are described, for example, in *Research Disclosure*, August 1979, item 18431. Support materials may also be treated or annealed to reduce shrinkage and promote dimensional stability. A method of making dimensionally stable polyester films is described in *Research Disclosure*, September 1999, item 42536.

10 It is also useful to use supports comprising dichroic mirror layers wherein the dichroic mirror layer reflects radiation at least having the predetermined range of wavelengths to the emulsion layer and transmits radiation having wavelengths outside the predetermined range of wavelengths. Such dichroic supports are described in U.S. Patent 5,795,708 (Boutet), incorporated  
15 herein by reference.

It is further possible to use transparent, multilayer, polymeric supports comprising numerous alternating layers of at least two different polymeric materials. Such multilayer polymeric supports preferably reflect at least 50% of actinic radiation in the range of wavelengths to which the photothermo-  
20 graphic material is sensitive, and provide photothermographic materials having increased speed. Such transparent, multilayer, polymeric supports are described in U.S. Patent 6,630,283 (Simpson et al.) that is incorporated herein by reference.

Opaque supports such as dyed polymeric films and resin-coated papers that are stable to high temperatures can also be used.

25 Support materials can contain various colorants, pigments, antihalation or acutance dyes if desired. For example, blue-tinted supports are particularly useful for providing images useful for medical diagnosis. Support materials may be treated using conventional procedures (such as corona discharge) to improve adhesion of overlying layers, or subbing or other adhesion-promoting  
30 layers can be used. Useful subbing layer formulations include those

conventionally used for photographic materials such as vinylidene halide polymers.

### **Photothermographic Formulations**

5                    Photothermographic materials of the invention can contain plasticizers and lubricants such as polyalcohols and diols of the type described in U.S. Patent 2,960,404 (Milton et al.), fatty acids or esters such as those described in U.S. Patent 2,588,765 (Robijns) and U.S. Patent 3,121,060 (Duane), and  
10                    silicone resins such as those described in GB 955,061 (DuPont). The materials can also contain matting agents such as starch, titanium dioxide, zinc oxide, silica, and polymeric beads including beads of the type described in U.S. Patent 2,992,101 (Jelley et al.) and U.S. Patent 2,701,245 (Lynn). Polymeric fluorinated surfactants may also be useful in one or more layers of the photothermographic materials for various purposes, such as improving coatability and optical density  
15                    uniformity as described in U.S. Patent 5,468,603 (Kub).

                    U.S. Patent 6,436,616 (Geisler et al.) describes various means of modifying photothermographic materials to reduce what is known as the “woodgrain” effect, or uneven optical density. This effect can be reduced or eliminated by several means, including treatment of the support, adding matting  
20                    agents to the topcoat, using acutance dyes in certain layers or other procedures described therein.

                    The photothermographic materials of this invention can include one or more antistatic agents in any of the layers including the photothermographic emulsion layer, or in separate conductive layers, on either or both sides of the  
25                    support. Thus, conductive components include, but are not limited to, soluble salts (for example, chlorides or nitrates), evaporated metal layers, or ionic polymers such as those described in U.S. Patent 2,861,056 (Minsk) and U.S. Patent 3,206,312 (Serman et al.), or insoluble inorganic salts such as those described in U.S. Patent 3,428,451 (Trevoy), electroconductive underlayers such  
30                    as those described in U.S. Patent 5,310,640 (Markin et al.), electronically-conductive metal antimonate particles such as those described in U.S. Patent

5,368,995 (Christian et al.), and electrically-conductive metal-containing particles dispersed in a polymeric binder such as those described in EP 0 678 776 A1 (Melpolder et al.). Particularly conductive particles also include the non-acicular metal antimonate particles described in copending and commonly assigned U.S.

5 Serial No. 10/304,224 (filed on November 27, 2002 by LaBelle, Sakizadeh, Ludemann, Bhavé, and Pham). All of the above patents and patent applications are incorporated herein by reference. Other antistatic agents are well known in the art.

Still other conductive compositions include one or more fluoro-  
10 chemicals each of which is a reaction product of  $R_f-CH_2CH_2-SO_3H$  with an amine wherein  $R_f$  comprises 4 or more fully fluorinated carbon atoms. These antistatic compositions are described in more detail in copending and commonly assigned U.S. Published Application 2003-0198901 (Sakizadeh et al.) that is incorporated herein by reference.

15 Additional conductive compositions include one or more fluoro-chemicals having the structure  $R_f-R-N(R'_1)(R'_2)(R'_3)^+ X^-$  wherein  $R_f$  is a straight or branched chain perfluoroalkyl group having 4 to 18 carbon atoms,  $R$  is a divalent linking group comprising at least 4 carbon atoms and a sulfide group in the chain,  $R'_1$ ,  $R'_2$ ,  $R'_3$  are independently hydrogen or alkyl groups or any two of  
20  $R'_1$ ,  $R'_2$ , and  $R'_3$  taken together can represent the carbon and nitrogen atoms necessary to provide a 5- to 7-membered heterocyclic ring with the cationic nitrogen atom, and  $X^-$  is a monovalent anion. These antistatic compositions are described in more detail in copending and commonly assigned U.S. Serial No. 10/265,058 (filed October 4, 2002 by Sakizadeh, LaBelle, and Bhavé) that is  
25 incorporated herein by reference.

The photothermographic materials of this invention can be constructed of one or more layers on a support. Single layer materials should contain the photocatalyst, the non-photosensitive source of reducible silver ions, the ascorbic acid or reductone reducing agent, the polycarboxylic acid compound,  
30 the binder, as well as optional materials such as toners, acutance dyes, coating aids and other adjuvants.

Two-layer constructions comprising a single imaging layer coating containing all the ingredients and a surface protective topcoat are generally found in the materials of this invention. However, two-layer constructions containing photocatalyst and non-photosensitive source of reducible silver ions in one  
5 imaging layer (usually the layer adjacent to the support) and the ascorbic acid or reductone reducing agent and the polycarboxylic acid compound in the second imaging layer or distributed between both layers are also envisioned.

For double-sided photothermographic materials, each side of the support can include one or more of the same or different imaging layers,  
10 interlayers, and protective topcoat layers. In such materials preferably a topcoat is present as the outermost layer on both sides of the support. The thermally developable layers on opposite sides can have the same or different construction and can be overcoated with the same or different protective layers. The polycarboxylic acid compound(s) can be the same or different on opposite sides of  
15 the support.

Layers to promote adhesion of one layer to another in photothermographic materials are also known, as described for example in U.S. Patent 5,891,610 (Bauer et al.), U.S. Patent 5,804,365 (Bauer et al.), and U.S. Patent 4,741,992 (Przezdziecki). Adhesion can also be promoted using specific  
20 polymeric adhesive materials as described for example in U.S. Patent 5,928,857 (Geisler et al.).

Layers to reduce emissions from the film may also be present, including the polymeric barrier layers described in U.S. Patent 6,352,819 (Kenney et al.), U.S. Patent 6,352,820 (Bauer et al.), and U.S. Patent 6,420,102 (Bauer et  
25 al.), all incorporated herein by reference.

Photothermographic formulations described herein can be coated by various coating procedures including wire wound rod coating, dip coating, air knife coating, curtain coating, slide coating, or extrusion coating using hoppers of the type described in U.S. Patent 2,681,294 (Beguín). Layers can be coated one at  
30 a time, or two or more layers can be coated simultaneously by the procedures described in U.S. Patent 2,761,791 (Russell), U.S. Patent 4,001,024 (Dittman et



al.), U.S. Patent 4,569,863 (Keopke et al.), U.S. Patent 5,340,613 (Hanzalik et al.),  
U.S. Patent 5,405,740 (LaBelle), U.S. Patent 5,415,993 (Hanzalik et al.), U.S.  
Patent 5,525,376 (Leonard), U.S. Patent 5,733,608 (Kessel et al.), U.S. Patent  
5,849,363 (Yapel et al.), U.S. Patent 5,843,530 (Jerry et al.), U.S. Patent 5,861,195  
5 (Bhave et al.), and GB 837,095 (Ilford). A typical coating gap for the emulsion  
layer can be from about 10 to about 750  $\mu\text{m}$ , and the layer can be dried in forced  
air at a temperature of from about 20°C to about 100°C. It is preferred that the  
thickness of the layer be selected to provide maximum image densities greater  
than about 0.2, and more preferably, from about 0.5 to 5.0 or more, as measured by  
10 a MacBeth Color Densitometer Model TD 504.

For example, after or simultaneously with application of the photo-  
thermographic emulsion formulation to the support, a protective overcoat layer  
formulation can be applied over the emulsion formulation. Preferably, the two  
formulations are applied simultaneously.

15 In other embodiments, a “carrier” layer formulation comprising a  
single-phase mixture of the two or more polymers described above may be applied  
directly onto the support and thereby located underneath the emulsion layer(s).  
Such formulations are described in U.S. Patent 6,355,405 (Ludemann et al.),  
incorporated herein by reference. Preferably, the carrier layer formulation is  
20 applied to the support simultaneously with application of the photothermographic  
emulsion layer formulation.

Mottle and other surface anomalies can be reduced in the  
photothermographic materials of this invention by incorporation of a fluorinated  
polymer as described for example in U.S. Patent 5,532,121 (Yonkoski et al.) or by  
25 using particular drying techniques as described, for example in U.S. Patent  
5,621,983 (Ludemann et al.).

Preferably, two or more layers are applied to a film support using  
slide coating. The first layer can be coated on top of the second layer while the  
second layer is still wet. The first and second fluids used to coat these layers can  
30 be the same or different solvents (or solvent mixtures).

While the first and second layers can be coated on one side of the film support, manufacturing methods can also include forming on the opposing or backside of said polymeric support, one or more additional layers, an antihalation layer, an antistatic or conductive layer, a layer containing a matting agent (such as silica), an imaging layer, a protective topcoat layer, or a combination of such layers. Alternatively, one backside layer can perform all of the desired functions.

It is also contemplated that the photothermographic materials of this invention can include thermally developable imaging (or emulsion) layers on both sides of the support and at least one heat-bleachable composition in an antihalation underlayer beneath layers on one or both sides of the support.

Photothermographic materials having thermally developable layers disposed on both sides of the support often suffer from “crossover.” Crossover results when radiation used to image one side of the photothermographic material is transmitted through the support and images the photothermographic layers on the opposite side of the support. Such radiation causes a lowering of image quality (especially sharpness). As crossover is reduced, the sharper becomes the image. Various methods are available for reducing crossover. Such “anti-crossover” materials can be materials specifically included for reducing crossover or they can be acutance or antihalation dyes. In either situation, when imaged with visible radiation, it is often necessary that they be rendered colorless during processing.

To promote image sharpness, photothermographic materials according to the present invention can contain one or more layers containing acutance, filter, crossover prevention (anti-crossover), anti-irradiation and/or antihalation dyes on one or both sides of the support. These dyes are chosen to have absorption close to the exposure wavelength and are designed to absorb non-absorbed or scattered light. One or more antihalation dyes may be incorporated into one or more antihalation layers according to known techniques, as an antihalation backing layer, as an antihalation underlayer, or as an antihalation overcoat. Additionally, one or more acutance dyes may be incorporated into one or more layers such as a thermally developable imaging layer, primer layer,

underlayer, or topcoat layer (particularly on the frontside) according to known techniques.

Dyes useful as antihalation, filter, crossover prevention (anti-crossover), anti-irradiation and/or acutance dyes include squaraine dyes described in U.S. Patent 5,380,635 (Gomez et al.), U.S. Patent 6,063,560 (Suzuki et al.), U.S. Patent 6,432,340 (Tanaka et al.), U.S. Patent 6,444,415 (Tanaka et al.), and EP 1 083 459 A1 (Kimura), the indolenine dyes described in EP 0 342 810 A1 (Leichter), and the cyanine dyes described in copending and commonly assigned U.S. Published Application 2003-0162134 (Hunt et al.). All of the above documents are incorporated herein by reference.

It is also useful in the present invention to employ compositions including acutance, filter, crossover prevention (anti-crossover), anti-irradiation and/or antihalation dyes that will decolorize or bleach with heat during processing. Dyes and constructions employing these types of dyes are described in, for example, U.S. Patent 5,135,842 (Kitchin et al.), U.S. Patent 5,266,452 (Kitchin et al.), U.S. Patent 5,314,795 (Helland et al.), U.S. Patent 6,306,566, (Sakurada et al.), U.S. Patent 6,306,566 (Sakurada et al.), JP Kokai 2001-142175 (Hanyu et al.), and JP 2001-183770 (Hanye et al.). Also useful are bleaching compositions described in JP Kokai 11-302550 (Fujiwara), JP Kokai 2001-109101 (Adachi), JP 2001-51371 (Yabuki et al.), JP Kokai 2001-22027 (Adachi), JP Kokai 2000-029168 (Noro), and U.S. Patent 6,376,163 (Goswami, et al.). All of the above references are incorporated herein by reference.

Particularly useful heat-bleachable backside antihalation compositions can include an infrared radiation absorbing compound such as an oxonol dye and various other compounds used in combination with a hexaarylbiimidazole (also known as a "HABI"), or mixtures thereof. Such HABI compounds are well known in the art, such as U.S. Patent 4,196,002 (Levinson et al.), U.S. Patent 5,652,091 (Perry et al.), and U.S. Patent 5,672,562 (Perry et al.), all incorporated herein by reference. Examples of such heat-bleachable compositions are described for example in U.S. Patent 6,455,210 (Irving et al.),

U.S. Patent 6,514,677 (Ramsden et al.), and U.S. Patent 6,558,880 (Goswami et al.), all incorporated herein by reference.

Under practical conditions of use, the compositions are heated to provide bleaching at a temperature of at least 90°C for at least 0.5 seconds.

- 5 Preferably bleaching is carried out at a temperature of from about 100°C to about 200°C for from about 5 to about 20 seconds. Most preferred bleaching is carried out within 20 seconds at a temperature of from about 110°C to about 150°C.

### **Imaging/Development**

- 10 The photothermographic materials of the present invention can be imaged in any suitable manner consistent with the type of material, using any suitable imaging source (typically some type of radiation or electronic signal). In some embodiments, the materials are sensitive to radiation in the range of from about at least 300 nm to about 1400 nm, and preferably from about 300 nm to  
15 about 850 nm. In one preferred embodiment, the materials are sensitive to radiation of from about 350 nm to about 450 nm.

- Imaging can be achieved by exposing the photothermographic materials of this invention to a suitable source of radiation to which they are sensitive, including ultraviolet radiation, visible light, near infrared radiation and  
20 infrared radiation to provide a latent image. Suitable exposure means are well known and include sources of radiation, including: incandescent or fluorescent lamps, xenon flash lamps, lasers, laser diodes, light emitting diodes, infrared lasers, infrared laser diodes, infrared light-emitting diodes, infrared lamps, or any other ultraviolet, visible, or infrared radiation source readily apparent to one  
25 skilled in the art, and others described in the art, such as in *Research Disclosure*, September, 1996, item 38957. Particularly useful infrared exposure means include laser diodes, including laser diodes that are modulated to increase imaging efficiency using what is known as multi-longitudinal exposure techniques as described in U.S. Patent 5,780,207 (Mohapatra et al.). Other exposure techniques  
30 are described in U.S. Patent 5,493,327 (McCallum et al.).

In some embodiments, the photothermographic materials of the present invention can be imaged using an imaging assembly comprising an X-radiation imaging source and one or more X-ray sensitive phosphor intensifying screens adjacent to the photothermographic material. Suitable X-radiation  
5 imaging sources include, for example, general medical, mammographic, dental, industrial X-ray units.

In some embodiments, the photothermographic materials of the present invention can be imaged directly using any X-radiation imaging source to provide a latent image.

10 In some embodiments, the photothermographic materials of the present invention can be imaged using an X-radiation imaging source and one or more X-ray sensitive prompt emitting or storage phosphors incorporated within the photothermographic material.

Thermal development conditions will vary, depending on the  
15 construction used but will typically involve heating the imagewise exposed material at a suitably elevated temperature. Thus, the latent image can be developed by heating the exposed material at a moderately elevated temperature of, for example, from about 50°C to about 250°C (preferably from about 80°C to about 200°C and more preferably from about 100°C to about 200°C) for a  
20 sufficient period of time, generally from about 1 to about 120 seconds. Heating can be accomplished using any suitable heating means such as a hot plate, a steam iron, a hot roller or a heating bath.

In some methods, the development is carried out in two steps. Thermal development takes place at a higher temperature for a shorter time (for  
25 example at about 150°C for up to 10 seconds), followed by thermal diffusion at a lower temperature (for example at about 80°C) in the presence of a transfer solvent.

#### **Use as a Photomask**

30 In some embodiments, the photothermographic materials of the present invention are sufficiently transmissive in the range of from about 350 to

about 450 nm in non-imaged areas to allow their use in a method where there is a subsequent exposure of an ultraviolet or short wavelength visible radiation sensitive imageable medium. For example, imaging the photothermographic material and subsequent development affords a visible image. The heat-developed  
5 photothermographic material absorbs ultraviolet or short wavelength visible radiation in the areas where there is a visible image and transmits ultraviolet or short wavelength visible radiation where there is no visible image. The heat-developed material may then be used as a mask and positioned between a source of imaging radiation (such as an ultraviolet or short wavelength visible radiation  
10 energy source) and an imageable material that is sensitive to such imaging radiation, such as a photopolymer, diazo material, photoresist, or photosensitive printing plate. Exposing the imageable material to the imaging radiation through the visible image in the exposed and heat-developed photothermographic material provides an image in the imageable material. This method is particularly useful  
15 where the imageable medium comprises a printing plate and the photothermographic material serves as an imagesetting film.

Thus, in one embodiment, the present invention provides a method comprising:

- A) imagewise exposing a photothermographic material of the present  
20 invention to electromagnetic radiation to form a latent image, and
- B) simultaneously or sequentially, heating the exposed photothermographic material to develop the latent image into a visible image.

Where the photothermographic material comprises a transparent support, this image-forming method can further comprise:

- 25 C) positioning the exposed and heat-developed photothermographic material with the visible image therein between a source of imaging radiation and an imageable material that is sensitive to the imaging radiation, and
- D) exposing the imageable material to the imaging radiation through  
30 the visible image in the exposed and heat-developed photothermographic material to provide an image in the imageable material.

### Imaging Assemblies

In preferred embodiments, the photothermographic materials of this invention are used in association with one or more phosphor intensifying screens and/or metal screens in what is known as "imaging assemblies." An intensifying  
5 screen absorbs X-radiation and emits longer wavelength electromagnetic radiation that the photosensitive silver halide more readily absorbs. Double-coated X-radiation sensitive photothermographic materials (that is, materials having one or more thermally developable imaging layers on both sides of the support) are preferably used in combination with two intensifying screens, one screen in the  
10 "front" and one screen in the "back" of the material.

The imaging assemblies of the present invention are composed of a photothermographic material as defined herein (particularly one sensitive to X-radiation or visible light) and one or more phosphor intensifying screens adjacent the front and/or back of the material. The screens are typically designed  
15 to absorb X-rays and to emit electromagnetic radiation having a wavelength greater than 300 nm.

There are a wide variety of phosphors known in the art that can be formulated into phosphor intensifying screens, including but not limited to, the phosphors described in, for example, *Research Disclosure*, Vol. 184, August 1979,  
20 Item 18431, Section IX, X-ray Screens/Phosphors, and U.S. Patent 2,303,942 (Wynd et al.), U.S. Patent 2,725,704 (Swindells), U.S. Patent 3,418,246 (Royce), U.S. Patent 3,428,247 (Yocon), U.S. Patent 3,591,516 (Rabatin), U.S. Patent 3,607,770 (Rabatin), U.S. Patent 3,617,743 (Rabatin), U.S. Patent 3,666,676 (Rabatin), U.S. Patent 3,725,704 (Buchanan et al.), U.S. Patent 3,778,615  
25 (Luckey), U.S. Patent 3,795,814 (Rabatin), U.S. Patent 3,974,389 (Ferri et al.), U.S. Patent 4,032,471 (Luckey), U.S. Patent 4,225,653 (Brixner et al.), U.S. Patent 4,226,653 (Brixner), U.S. Patent 4,311,487 (Luckey et al.), U.S. Patent 4,368,390 (Takahashi et al.), U.S. Patent 4,387,141 (Patten), (Bunch et al.), U.S. Patent 4,405,691 (Yale), U.S. Patent 4,835,397 (Arakawa et al.), U.S. Patent 4,865,944  
30 (Roberts et al.), U.S. Patent 4,994,355 (Dickerson et al.), U.S. Patent 4,997,750 (Dickerson et al.), U.S. Patent 5,021,327, U.S. Patent 5,064,729 (Zegarski), U.S.

Patent 5,108,881 (Dickerson et al.), U.S. Patent 5,227,253 (Takasu et al), U.S. Patent 5,250,366 (Nakajima et al.), U.S. Patent 5,381,015 (Dooms), U.S. Patent 5,464,568 (Bringley et al.), U.S. Patent 5,626,957 (Benso et al.), U.S. Patent 5,871,892 (Dickerson et al.), and EP 0 491 116A1 (Benzo et al.), the disclosures of  
5 which are all incorporated herein by reference for their teaching of phosphors and or for the formulation of phosphor intensifying screens.

Phosphor intensifying screens can take any convenient form providing they meet all of the usual requirements for use in radiographic imaging, as described for example in U.S. Patent 5,021,327 (Bunch et al.), incorporated  
10 herein by reference. A variety of such screens are commercially available from several sources including but not limited to, LANEX<sup>®</sup>, X-SIGHT<sup>®</sup> and INSIGHT<sup>®</sup> Skeletal screens all available from Eastman Kodak Company. The front and back screens can be appropriately chosen depending upon the type of emissions desired, the desired photicity, emulsion speeds, and percent crossover. A metal (such as  
15 copper or lead) screen can also be included if desired.

Imaging assemblies can be prepared by arranging a suitable photo-thermographic material in association with one or more phosphor intensifying screens, and one or more metal screens in a suitable holder (often known as a cassette), and appropriately packaging them for transport and imaging uses.

20 Constructions and assemblies useful in industrial radiography include, for example, U.S. Patent 4,480,024 (Lyons et al), U.S. Patent 5,900,357 (Feumi-Jantou et al.), and EP 1 350 883 A1 (Pesce et al.).

The following examples are provided to illustrate the practice of the present invention and the invention is not meant to be limited thereby.

25

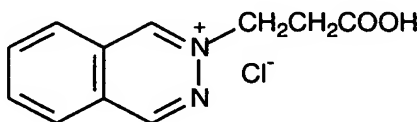
#### **Materials and Methods for the Examples:**

All materials used in the following examples are readily available from standard commercial sources, such as Aldrich Chemical Co. (Milwaukee, WI) unless otherwise specified. All percentages are by weight unless otherwise  
30 indicated. The following additional materials were prepared and used as follows.



ZONYL<sup>®</sup> FSN is a nonionic fluorosurfactant that is available from E. I. DuPont de Nemours & Co. (Wilmington, DE). It is a fluorinated polyethyleneoxide alcohol.

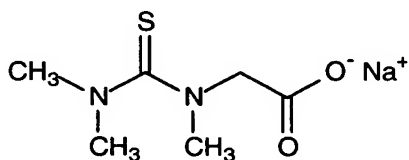
Compound A-1 is the chloride salt of the reaction product of acrylic acid and phthalazine. It is shown as compound (I-1) in commonly assigned U.S. Patent 6,605,418 (Ramsden et al.) noted above. It is believed to have the structure shown below.



A-1

10

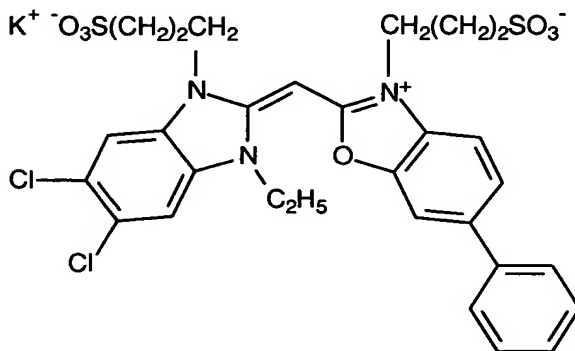
Compound SS-1a is described in U.S. Patent 6,296,998 (Eikenberry et al.) and is believed to have the structure shown below.



SS-1a

15

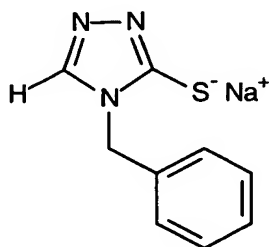
Blue sensitizing dye SSD-1 is believed to have the structure shown below.



SSD-1

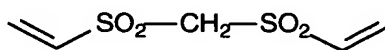
20

Compound T-1 is the sodium salt of 2,4-dihydro-4-(phenylmethyl)-3H-1,2,4-triazole-3-thione. It is believed to have the structure shown below. It is drawn as the sodium salt of the thiol form but may also exist as the sodium salt of the thione tautomer.



T-1

Bisvinyl sulfonyl methane (VS-1) is 1,1'-(methylenebis(sulfonyl))-bis-ethene. It can be prepared as described in EP 0 640 589 A1 (Gathmann et al.) and is believed to have the structure shown below.



VS-1

#### **Example 1 – Preparation of Aqueous-Based Photothermographic Materials:**

Aqueous-based photothermographic materials of this invention were prepared in the following manner.

##### **Preparation of Silver Benzotriazole Dispersion:**

Solution A was prepared in a stirred reaction vessel by dissolving 85 g of lime-processed gelatin, 25 g of phthalated gelatin, in 2000 g of deionized water.

Solution B containing 185 g of benzotriazole, 1405 g of deionized water, and 680 g of 2.5 molar sodium hydroxide was prepared. The mixture in the reaction vessel was adjusted to a pAg of 7.25 and a pH of 8.0 by addition of 2.5 molar sodium hydroxide solution as needed, and maintaining it at temperature of 36°C.

Solution C containing 228.5 g of silver nitrate and 1222 g of deionized water was added to the reaction vessel at an accelerated flow rate defined by:  $\text{Flow} = 16(1 + 0.002t^2)$  ml/min (where  $t$  is the time in minutes), and the pAg was maintained at 7.25 by simultaneous addition of Solution B. This process was terminated when Solution C was exhausted, at which point Solution D containing 80 g of phthalated gelatin and 700 g of deionized water at 40°C was added to the reaction vessel. The mixture was then stirred and the pH was adjusted to 2.5 with 2 molar sulfuric acid to coagulate the silver salt emulsion. The coagulum was washed twice with 5 liters of deionized water, and redispersed by adjusting pH to 6.0 and pAg to 7.0 with 2.5 molar sodium hydroxide solution and Solution B. The resulting dispersion contained fine particles of silver benzotriazole.

#### Preparation of Tabular Grain Silver Halide Emulsions:

A reaction vessel equipped with a stirrer was charged with 6 liters of water containing 4.21 g of lime-processed bone gelatin, 4.63 g of sodium bromide, 37.65 mg of potassium iodide, an antifoamant, and 1.25 ml of 0.1 molar sulfuric acid. The solution was then held at 39°C for 5 minutes. Simultaneous additions were then made of 5.96 ml of 2.5378 molar silver nitrate and 5.96 ml of 2.5 molar sodium bromide over 4 seconds. Following nucleation, 0.745 ml of a 4.69% solution of sodium hypochlorite was added. The temperature was increased to 54°C over 9 minutes. After a 5-minute hold, 100 g of oxidized methionine lime-processed bone gelatin in 1.412 liters of water containing additional antifoamant at 54°C were then added to the reactor. The reactor temperature was held for 7 minutes, after which 106 ml of 5 molar sodium chloride containing 2.103 g of sodium thiocyanate were added. The reaction was continued for 1 minute.

During the next 38 minutes, the first growth stage took place wherein solutions of 0.6 molar  $\text{AgNO}_3$ , 0.6 molar sodium bromide, and a 0.29 molar suspension of silver iodide (Lippmann) were added to maintain a nominal uniform iodide level of 4.2 mole %. The flow rates during this growth

segment were increased from 9 to 42 ml/min (silver nitrate) and from 0.8 to 3.7 ml/min (silver iodide). The flow rates of the sodium bromide were allowed to fluctuate as needed to maintain a constant pBr. At the end of this growth segment 78.8 ml of 3.0 molar sodium bromide were added and held for 3.6 minutes.

5                    During the next 75 minutes the second growth stage took place wherein solutions of 3.5 molar silver nitrate and 4.0 molar sodium bromide and a 0.29 molar suspension of silver iodide (Lippmann) were added to maintain a nominal iodide level of 4.2 mole %. The flow rates during this segment were increased from 8.6 to 30 ml/min (silver nitrate) and from 4.5 to 15.6 ml/min  
10 (silver iodide). The flow rates of the sodium bromide were allowed to fluctuate as needed to maintain a constant pBr.

                    During the next 15.8 minutes, the third growth stage took place wherein solutions of 3.5 molar silver nitrate, 4.0 molar sodium bromide, and a 0.29 molar suspension of silver iodide (Lippmann) were added to maintain a  
15 nominal iodide level of 4.2 mole %. The flow rates during this segment were 35 ml/min (silver nitrate) and 15.6 ml/min (silver iodide). The temperature was decreased to 47.8°C during this addition segment.

                    During the next 32.9 minutes, the fourth growth stage took place wherein solutions of 3.5 molar silver nitrate and 4.0 molar sodium bromide and a  
20 0.29 molar suspension of silver iodide (Lippmann) were added to maintain a nominal iodide level of 4.2 mole %. The flow rates during this segment were held constant at 35 ml/min (silver nitrate) and 15.6 ml/min (silver iodide). The temperature was decreased to 35°C during this segment.

                    A total of 12 moles of silver iodobromide (4.2% bulk iodide) were  
25 formed. The resulting emulsion was coagulated using 430.7 g of phthalated lime-processed bone gelatin and washed with de-ionized water. Lime-processed bone gelatin (269.3 g) was added along with a biocide and pH and pBr were adjusted to 6 and 2.5 respectively.

                    The resulting emulsion was examined by Scanning Electron  
30 Microscopy. Tabular grains accounted for greater than 99% of the total projected

area. The mean ECD of the grains was 2.369  $\mu\text{m}$ . The mean tabular thickness was 0.062  $\mu\text{m}$ .

This emulsion was further sensitized using a combination of a gold sensitizer (potassium tetrachloroaurate) and a sulfur sensitizer (compound SS-1a) at 60°C for 10 minutes, and 1.0 mmol of blue sensitizing dye SSD-1 per mole of silver halide was added before the chemical sensitizers.

Preparation of Photothermographic Materials:

Solution A: Silver benzotriazole and gelatin (35% gelatin/65% water) were placed in a beaker and heated to 50°C for 15 minutes to melt the material. A 5% aqueous solution of 3-methylbenzothiazolium iodide was added. Mixing for 15 minutes was followed by cooling to 40°C. The sodium salt of benzotriazole was added and the mixture was stirred for 15 minutes. Compound T-1 was then added. Mixing for 15 minutes was followed by addition of 2.5 N sulfuric acid to adjust the pH to 5.5. Zonyl FSN surfactant was then added.

Solution B: A portion of the tabular-grain silver halide emulsion prepared above was placed in a beaker and melted by heating at 40°C.

Solution C: Solution C was prepared by adding the dry materials to water and heating to 40°C. All polycarboxylic acids were added at an equimolar level. The amount of polycarboxylic acid added was 0.5 moles of acid per 1.0 mol silver halide.

Solutions A, B, and C were mixed immediately before coating to form a photothermographic emulsion formulation. Each formulation was coated as a single layer on a 7 mil (178  $\mu\text{m}$ ) transparent, blue-tinted poly(ethylene terephthalate) film support using a conventional automated knife coating machine to form an imaging layer having the dry composition shown below in TABLE I. Samples were dried at 125°F (51.7°C) for 6.5 minutes. A control sample (Sample 1-1) was prepared using the same components, but omitting the polycarboxylic acid compound.

TABLE I – Photothermographic Emulsion Prepared from  
Tabular Silver Halide Grains

Solution	Component	Dry Coating Weight (g/m <sup>2</sup> )
A	Silver (from Ag benzotriazole salt)	2.00
A	Lime processed gelatin	1.10
A	3-Methylbenzothiazolium Iodide	0.09
A	Sodium benzotriazole	0.10
A	Mercaptotriazole compound T-1	0.07
A	Zonyl FSN	0.06
B	Silver (from AgBrI emulsion)	0.40
C	Succinimide	0.13
C	Dimethylurea	0.16
C	Phthalazine Compound A-1	0.06
C	Compound VS-A	0.06
C	Ascorbic Acid	1.86
C	Polycarboxylic acid Compound	See TABLE II

Evaluation of Photothermographic Materials:

5                   The resulting photothermographic films were imagewise exposed for  $10^{-2}$  seconds using an EG&G flash sensitometer equipped with a P-16 filter and a 0.7 neutral density filter. Following exposure, the films were developed by heating on a heated rotating drum for 18 seconds at 150°C to generate continuous tone wedges. These samples provided initial  $D_{min}$ ,  $D_{max}$  and Relative Speed.

10                   Densitometry measurements were made on a custom built computerized scanning-densitometer that meets ISO Standards 5-2 and 5-3 and

takes an optical density reading every 0.33 mm. The results are believed to be comparable to measurements from commercially available densitometers.

Density of the wedges was measured using a filter appropriate to the sensitivity of the photothermographic material to obtain graphs of density  
5 versus log exposure (that is, D log E curves).  $D_{min}$  is the density of the non-exposed areas after development and it is the average of the eight lowest density values.

Duplicate unexposed/unprocessed sample strips were packaged in breathable black polyester bags and aged in a room held at 70°F (21°C)/50%RH.  
10 This temperature and humidity represent natural aging conditions. After 10 weeks, the strips were exposed for  $10^{-2}$  seconds using an EG&G flash sensitometer equipped with a P-16 filter and a 0.7 neutral density filter. Following exposure, the films were developed using a heated rotating drum for 18 seconds at 150°C. The sensitometry obtained from these strips was then compared to the  
15 initial sensitometry.

The results, shown below in TABLE II record the initial sensitometry, and change in  $D_{min}$  ( $\Delta D_{min}$ ) after 10 weeks of natural aging. They demonstrate that polycarboxylic acids described herein and used according to the present invention help minimize increase in  $D_{min}$  when compared to a control  
20 sample from which the polycarboxylic acid had been omitted or to a film sample containing a polycarboxylic acid outside the scope of the present invention (for example, a monocarboxylic acid).

The speeds are reported as “relative speed.” “Relative Speed-2” was determined at a density value 1.00 above  $D_{min}$ . Speed values were  
25 normalized. Sample 1-1, which had no acid compound added, and was assigned a relative speed value of 100.

TABLE II

Sample	Acid Compound Added	Dmin	Dmax	Relative Speed-2	$\Delta$ Dmin After 10 Weeks Aging	pKa of acid	Number of COOH groups on acid	Invention (I) or Comparison (C)
1-1	none	0.27	2.571	100	1.747	—	—	C
1-2	Citric Acid	0.264	2.468	64	0.519	3.14	3	I
1-3	Tricarballic Acid	0.285	2.455	139	0.693	3.67	3	I
1-4	1,2,3,4-butane tetracarboxylic acid	0.264	2.226	41	0.706	3.43	4	I
1-5	L-tartaric acid	0.267	2.433	79	0.731	2.98	2	I
1-6	Succinic acid	0.291	2.414	204	0.854	4.19	2	I
1-7	Lactic acid	0.291	2.530	183	1.569	3.08	1	C
1-8	Phthalic acid	0.269	2.636	88	0.654	2.89	2	I



Sample	Acid Compound Added	Dmin	Dmax	Relative Speed-2	$\Delta$ Dmin After 10 Weeks Aging	pKa of acid	Number of COOH groups on acid	Invention (I) or Comparison (C)
1-9	Salicylic acid	0.263	2.310	75	1.127	2.98	1	C
1-10	2,4-dihydroxy-benzoic acid	0.278	2.444	73	1.060	3.29	1	C
1-11	Hemimellitic acid	0.258	2.110	28	0.269	2.80	3	I

**Example 2    Evaluation of Polycarboxylic Acid Levels:**

Photothermographic compositions of this invention were prepared by mixing solutions/emulsions containing the components described in TABLE I. The ratio of materials remained the same as in TABLE I but the total silver coating weight was reduced in these examples to 2.1 g/m<sup>2</sup> (The total silver coating weight includes silver from Ag benzotriazole plus silver from silver halide emulsion). Citric acid was tested at three levels. The amounts added were 0.25, 0.50 and 1.0 mole citric acid to 1.0 mole silver halide.

Each composition was coated as a single layer on a 7 mil (178 µm) transparent, blue-tinted poly(ethylene terephthalate) film support using a conventional automated knife coating machine. Samples were dried at 116°F (46.6°C) for 8.0 minutes. A control sample (Sample 2-1) was prepared using the same components, but omitting citric acid.

The resulting photothermographic films were imagewise exposed and developed as described in Example 1. The results, shown below in TABLE III, record the initial sensitometry and change in Dmin (Δ Dmin) after 4 weeks of shelf aging. They demonstrate that polycarboxylic acids described herein help minimize the Dmin increase over time when compared to a control sample from which the polycarboxylic acid had been omitted. The results also demonstrate that the level of the polycarboxylic acid can be further optimized if desired.

The speeds are reported as “relative speed.” “Relative Speed-2” was determined at a density value 1.00 above Dmin. Speed values were normalized. Sample 2-1, which had no citric acid added, was assigned a relative speed value of 100.

TABLE III

Sample	Moles of Citric Acid per mole of Silver Halide	D <sub>min</sub>	D <sub>max</sub>	Relative Speed-2	Δ D <sub>min</sub> After 4 Weeks Aging	Invention (I) or Comparison (C)
2-1	none	0.289	2.47	100	2.149	C
2-2	0.25	0.280	2.39	115	0.192	I
2-3	0.5	0.296	2.27	126	0.026	I
2-4	1.0	0.318	2.35	110	-0.016	I

The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.